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Evaluation of Methods for Hazardous Chemicals Listed in Appendix D to 40 CFR 122 (Table 5)

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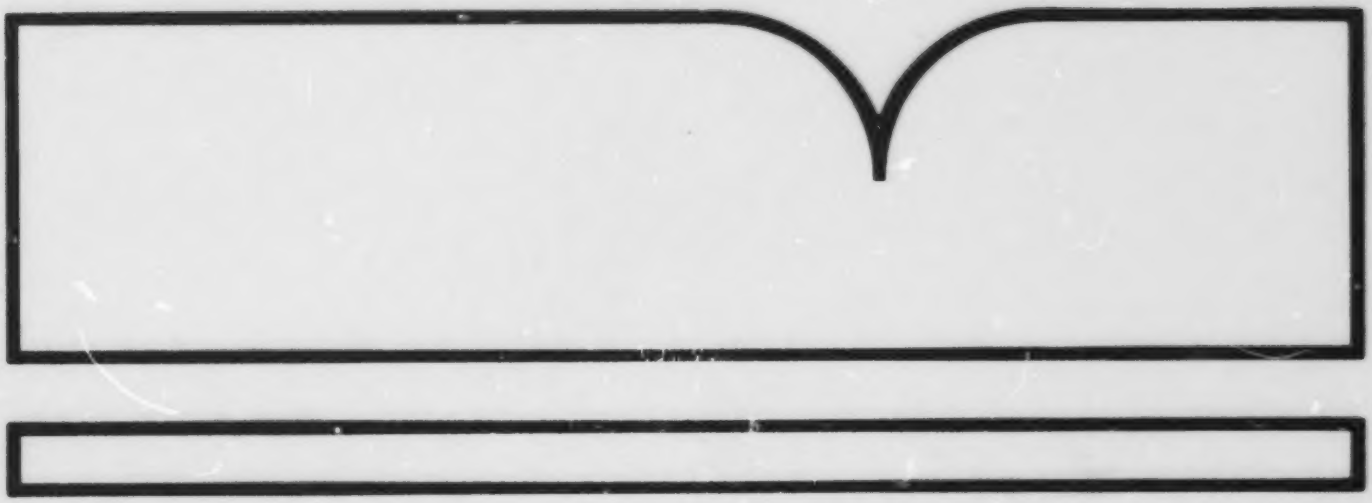

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EVALUATION OF METHODS FOR HAZARDOUS CHEMICALS LISTED IN APPENDIX D TO 40 CFR 122 (TABLE V)

by

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16. ABSTRACT

Of 75 organic compounds listed in Appendix D to 40 CRF 122 (Table V), 24 compounds have not been previously shown amenable to existing EPA Methods for analysis in water and wastewater. The present work reports on 17 of those 24 compounds using 600 Methods with appropriate modification. The approach was to demonstrate performance in the areas: (1) chromatography - using fused silica capillary columns, (2) extraction and concentration, and (3) cleanup. When attempts were successful, the integrated method was tested for accuracy and precision. Benzonitrile is effectively analyzed using Method 632. Kepone and dichlone are extracted using Method 608, and a modified Method 617 cleanup; overall recoveries are 15 percent and 52 percent. Quinoline is quantitatively recovered using the Method 625 extraction, but strychnine was recovered at 50 percent. Trichlorfon could not be analyzed using Method 622 due to hydrolysis. Six of the twelve organophosphorous pesticides decomposed using splitless capillary injection at 300°C. Methyl mercaptan is not analyzed by Method 601 (FID detection). Propylene oxide can be analyzed by Method 601/FID but does not perform well. Allyl alcohol shows poor performance using modified Method 603. A purge-and-trap approach was shown to have substantial problems with the volatile amines. An automated heated headspace/capillary column method worked poorly for monoalkyl amines. A specially prepared column packing was effective for all of the volatile amines. No method development was achieved for either ethanolamine or isopropanolamine.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, Ohio conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report presents the results of the evaluation of chromatographic methods for the analysis of toxic compounds listed in Appendix D to 40 CRF 122 (Table V).

Robert L. Booth, Director
Environmental Monitoring and
Support Laboratory-
Cincinnati, Ohio

ABSTRACT

Of 75 organic compounds listed in Appendix D to 40 CRF 122 (Table V), 24 compounds have not been previously shown amenable to an existing EPA method for analysis in water and wastewater. The present work reports on efforts to demonstrate analysis capability for 17 of those 24 compounds by applying existing 600-series methods with appropriate modification. In each case, a test analyte set for a given method/approach consisted of essentially all of the Appendix D Table V compounds belonging to that compound class. The approach was to separately demonstrate performance in the areas: (1) chromatography - using fused silica capillary columns when possible, (2) extraction and concentration, and (3) cleanup. Where all of these attempts were successful, the integrated method was tested for accuracy and precision, but the program scope did not permit a formal method validation study in those cases.

In summary, the findings are:

- Benzonitrile is effectively analyzed using neutral liquid-liquid extraction with methylene chloride, Florisil column cleanup, and fused silica gas chromatography (GC) with a nitrogen-specific detector

- Kepone and dichlone are effectively extracted using methylene chloride and can be recovered with a Florisil column cleanup. Overall recoveries, however, are low, for dichlone (15 percent) and kepone (52 percent), apparently due to instability during Kuderna-Danish (KD) distillation of the cleaned up fraction

- Quinoline is essentially quantitatively recovered using methylene chloride extraction at either neutral or basic pH, but the maximum recovery obtained for strychnine was only about 50 percent for those extraction solvents tried. Although strychnine was found to decompose during KD

distillation with some solvents, extractability seems to be the principal problem

- Trichlorfon could not be recovered using separatory funnel or reverse phase extraction procedures due, apparently, to decomposition in water. Six of the twelve organophosphorous compounds decomposed partially or substantially upon splitless capillary injection at 300°C

- Methyl mercaptan is not well analyzed by purge-and-trap GC with flame ionization detection (FID) and has an unacceptably high detection limit due to FID insensitivity and interference from methanol

- Propylene oxide can be analyzed by purge-and-trap GC-FID but does not perform as well as other analytes due to both decomposition in the trap and poor purging efficiency. Its performance is about the same using 85°C purging

- Allyl alcohol has very poor performance using purge-and-trap GC-FID due to poor purging efficiency and severe GC peak tailing

- A purge-and-trap approach was shown to have substantial, but not necessarily insurmountable, problems associated with adsorption of the volatile amines (methyl-, trimethyl-, ethyl-, diethyl-, triethyl-, and butyl-). An automated heated headspace/capillary column method worked well for trialkyl amines but poorly for monoalkyl amines. A specially prepared column packing was effective for all of the volatile amines

- No method development progress was achieved for either ethanolamine or isopropanolamine.

This report is submitted in fulfillment of U.S. EPA Contract 68-03-1760 Work Assignment 9 by Battelle's Columbus Laboratories. This report covers a period from May, 1984 to February, 1985 and was completed as of March, 1985.

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SECTION 1

INTRODUCTION

The objective of this research was to evaluate analytical methods for hazardous chemicals listed in Appendix D to 40 CFR 122 (Table V). This listing (reproduced in Appendix A) contains 75 organic chemicals that are required to be identified by existing dischargers if they are expected to be present. Standard analytical methods have been previously developed and validated by the EPA for most of the Appendix D/Table V chemicals (1). Of the 75 organic compounds of Table V, 24 compounds have not received analytical method development work, and these high-interest compounds are listed in Table 1. As indicated, seven of the high-interest compounds were eliminated by the Project Officer from method evaluation. In all such cases, prior experimentation and a literature search indicated that evaluation of methods for these compounds could not be successfully accomplished within the limited funding and time available for this work. A major objective of this work was to provide a minimum number of methods to cover a maximum number of Appendix D/Table V compounds to minimize the validation effort required after methods were developed. Accordingly, the Appendix D/Table V chemicals were divided into six chemical classes, each of which contained at least one of the high-interest compounds. These chemical classes include the following:

Organophosphorous compounds
Neutral nitrogen compounds
Chlorinated pesticides
Extractable semivolatile bases
Volatile compounds
Volatile amines and alcohol amines

The chemical class of each high-interest compound is identified in Table 1. In this work, methods were evaluated for all or nearly all of

TABLE 1. HIGH-INTEREST COMPOUNDS

High-interest Compound	Chemical Class
Allyl alcohol	Volatile compound
Benzonitrile	Neutral nitrogen compound
Butylamine	Amine
Dichlone	Chlorinated pesticide
2,2-Dichloropropionic acid	(Eliminated)
Diethylamine	Amine
Diquat	(Eliminated)
Ethanolamine	Amine
Isopropanolamine	Amine
Kepone	Chlorinated pesticide
methyl mercaptan	Volatile compound
Ethylamine	Amine
Methylamine	Amine
Naphthenic acid	(Eliminated)
Phenol sulfonate	(Eliminated)
Phosgene	(Eliminated)
Propargite	(Eliminated)
Propylene oxide	Volatile compound
Pyrethrins	(Eliminated)
Quinoline	Extractable semivol base
Strychnine	Extractable semivol base
Trichlorfon	Organophosphorous compound
Trimethylamine	Amine
Triethylamine	Amine

the Appendix D/Table V compounds of a given class to ensure that method modifications which enhanced performance for a high-interest analyte did not detract from the method performance already in place for the other compounds in the class. The volatile compounds class was augmented by an additional five compounds which were not in the Appendix D/Table V listing but were of interest to the EPA Project Officer. These compounds were acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl butyl ketone, and dioxane. To consolidate information on commerical sources and stated purities of the reagents and analytes used in this work, all such information appears in Appendix B rather than the individual "Experimental" sections.

This report is divided into nine sections, each of which provides experimental procedures, results and discussion, conclusions, and recommendations for one of the compound classes. The experimental design for each class incorporated independent evaluation of four aspects of a method: chromatographic separation, injection conditions, sample workup, and cleanup procedures. A main feature of the chromatographic separation evaluation was to test both polar and nonpolar fused silica capillary columns. Injection conditions tested included variable temperature evaporator cavity (split/splitless) injection and cold, on-column injection. Sample workup usually involved liquid-liquid extraction and extract concentration, while cleanup procedures emphasized Florisil column techniques. When reasonable results were obtained in each of these areas for a compound class, the precision and accuracy of an integrated method were tested. It must be emphasized that the research goal did not include performance of a formal method validation study, but was limited in scope to simply indicate whether an analytical method merited a future detailed method validation experiment.

SECTION 2

CONCLUSIONS

With only a few exceptions, the 17 high-interest compounds evaluated in this research are relatively intractable to the application of current EPA 600 Methods. The exceptions, i.e., compounds which can be analyzed using some combination of current methods, are:

- Benzonitrile
- Quinoline
- Propylene oxide by either the room temperature or 85°C purge-and-trap approach (modified methods 601 and 603, respectively). However, the propylene oxide data clearly indicate that this compound partially decomposes during trap desorption, and the result is that variable precision and accuracy might be expected without further method improvements.

A few of the 17 high-interest compounds were successfully analyzed reproducibly but not with high recoveries. For example:

- Strychnine was reliably recovered at about 50 percent using a number of extraction solvents with separatory funnel extraction procedures
- Kepone was recovered at about 50 percent overall using methylene chloride extraction with a Florisil cleanup procedure.

One analyte, trichlorfon, was simply not stable in water under any conditions, and, therefore, may not be of concern as a water-borne pollutant. Another analyte which exhibited an apparent stability problem was dichlone which was recovered at only 15 percent for the

integrated extraction/cleanup method (Method 608). In this case, decomposition in the cleanup step, either on Florisil or during solvent removal, was observed.

For the twelve neutral nitrogen compounds evaluated, only the high-interest analyte, benzonitrile, gave excellent analytical performance. The overall recoveries obtained for the nitrotoluenes, dinitrobenzenes and dichlobenil were generally acceptable at 70 to 80 percent (except 1,3-dinitrobenzene at 64 percent) with RSD% values of about 15 percent (except 1,4- and 1,3-dinitrobenzene).

Most of the problems associated with the purge-and-trap analyte sets were shown to be associated with decompositon, probably by hydrolysis, during trap desorption. Two additional problems were encountered with methyl mercaptan: (1) FID sensitivity was low, as expected, and (2) coelution with methanol, often present as a laboratory contaminant or spiking medium, significantly reduced its reproducibility. Both of these problems could be eliminated with a sulfur-specific detector. In the case of allyl alcohol, the modified Method 603 scheme suggested a detection limit on the order of 70 µg/L. This result was due to the very low purging efficiency (about 15 percent) at 85°C and the extreme GC peak tailing on the Method 601 column.

Based on extensive work, an 85°C purge/trap/desorb approach to volatile amine analysis is substantially hindered by trap/desorption problems and analyte adsorption in the purge-and-trap apparatus plumbing. The heated headspace sampling (HHS) approach that was studied seems to have some merit, but extensive modification of the sampler device on the Perkin-Elmer HS-100 would be required to eliminate all contact of the vapor sample with metal surfaces. Although it was not tested in the present work, use of a nitrogen selective detector would significantly improve the performance of the HHS approach. Chromatography problems with these very polar, basic species are not unacceptable using specially prepared packings or thick film capillary columns.

No progress was made on GC analysis of the extremely polar alcohol amines, and without a chromatographic determinative technique, no experiment on extraction/sample workup were possible.

In general, GC analysis of the semi-volatile analytes on fused silica capillary columns was successful for the Appendix D/Table V compounds which were not the high interest, Table 1, compounds, and only one case of coelution (chlorpyrifos and parathion) was observed. Capillary chromatography was less successful for the high-interest compounds, and the principal difficulty was some tendency toward decomposition in the evaporator cavity injector for captan, some of the organophosphorous pesticides and neutral nitrogen compounds (carbamides and ureas). It was shown that on-column injection can essentially eliminate that problem. The use of a very high polarity secondary column (Carbowax 20M) was unsuccessful in every case due to non-elution of many of the lower volatility analytes. A better choice for a secondary column would be one of the medium polarity silicone gum phases, e.g., OV-1701, OV-17, CP Sil 88 (Chrompac), SP-2340.

SECTION 3

RECOMMENDATIONS

Based on the research results obtained in this work, the following recommendations can be made:

- Use of nonpolar fused silica capillary columns provides good separation for the high priority semivolatile analytes, and further work to show reproducibility of response factors should be performed. Cold, on-column injection is recommended for organophosphorus pesticides, carbamides, and captan

- Benzonitrile can be analyzed using neutral liquid-liquid extraction with methylene chloride, Florisil column cleanup, and fused silica GC with a nitrogen-specific detector

- Quinoline and strychnine can be included in Method 625 whenever fused silica capillary chromatography is specified. However, a problem of poor extraction efficiency (50 percent) for strychnine needs some further work

- An analytical approach for the determination of trichlorfon could not be established since it apparently decomposes rapidly in water

- Decomposition of dichlone during solvent reduction deserves further investigation. Perhaps addition of an antioxidant or use of different extraction and/or cleanup solvents could eliminate this possible problem.

- Future method development effort for methyl mercaptan should involve a sulfur-specific detector such as the Hall electrolytic conductivity detector. A purge-and-trap approach will probably prove workable for methyl mercaptan

- Future purge-and-trap method development work on hydrolyzable analytes such as esters and epoxides should include a trap drying step preceding desorption. In addition, holding times for field samples must also be determined with regard to the effect of temperature and pH on the stability of these analytes toward hydrolysis

- Future method development for allyl alcohol should include a capillary column or packed column known to perform well for alcohols in the determinative step to avoid GC peak tailing. A heated purge-and-trap approach is recommended, even though the purging efficiency is low

- Future method development work for amines and alcohol amines should include ion chromatography with and without an ion exchange, distillation or evaporative pre-concentration step. Future work on purge-and-trap based methods must address the fairly difficult problems of analyte adsorption in the transfer lines and the identification of an appropriate trapping medium from which nanogram levels can be reliably desorbed. For GC-based methodology, future work on a heated headspace sampling approach has some merit, but it also must address the problem of adsorption on metallic parts of the sampling system and transfer line. Polar thick film fused silica capillary columns may perform better than the nonpolar column used in this work, and they are recommended for future GC based methods for these compounds. All GC based method development should be designed to use nitrogen-specific detection.

SECTION 4

ORGANOPHOSPHOROUS COMPOUNDS

Trichlorfon is the only organophosphorous compound of the high-interest chemicals (Table 1), and it was evaluated with 11 other organophosphorous compounds cited in Appendix D to 40 CFR 122. These compounds include:

- Chlorpyrifos
- Coumaphos
- Diazinon
- Disulfoton
- Ethion
- Guthion
- Malathion
- Methyl parathion
- Mevinphos
- Naled
- Parathion

EXPERIMENTAL

Chromatographic Separations

Chromatographic (GC) separations of the organophosphorous compounds were evaluated on both a SPB-5 and a Carbowax 20M fused silica capillary column using the instrumentation and conditions described in Table 2. Analytes were injected individually and in mixtures in appropriate injection solvents, generally at 50 µg/mL.

Evaluation of Injection Conditions

The evaluation of standard heated evaporator cavity injections at temperatures of 200, 250, and 300°C was performed using the SPB-5 column with the same instrumentation and conditions described in Table 2, except that split rather than splitless injection was used.

TABLE 2. INSTRUMENTATION AND CONDITIONS FOR GC ANALYSES WITH SPB-5 AND CARBOWAX 20M FUSED SILICA CAPILLARY COLUMNS

Instrumentation/ Conditions	SPB-5 Column Analysis	Carbowax 20M Column Analysis
Gas chromatograph	Hewlett-Packard Model 5730	Hewlett-Packard Model 5730
Detector	FID	FID
Column	SPB-5 fused silica capillary, 30 m x 0.25 mm ID with a 0.25 µm film thickness (Supelco, Inc., Bellefonte, PA)	Carbowax 20M fused silica capillary, 30 m x 0.25 mm ID with a 0.25 µm film thickness (Supelco, Inc.)
Carrier	Hydrogen at 50 cm/sec room temperature	Hydrogen at 50 cm/sec room temperature
Detector Temperature	300°C	300°C
Injection Temperature	300°C	300°C
Injection Volume	2 µL, splitless (45 sec)	2 µL, splitless (45 sec)
Temperature Program	70°C (4 min hold); 8°C/min to 300°C (8 min hold)	70°C (4 min hold); 8°C/min to 240°C (8 min hold)

Identification of decomposition products and elution order confirmations for these compounds were performed using gas chromatography/mass spectrometry (GC/MS) with the following conditions:

GC:	- Carlo Erba Model 4160 with 280°C injector temperature
MS:	- Finnigan Model 3200
GC Column:	- DB-5 fused silica capillary 30 m x 0.25 mm ID with a 0.25 µm film thickness
Column Temperature Program:	- 70°C (4 min hold); 8°C/min to 300°C (8 min hold)
Injection Volume:	- 2 µL splitless (45 sec)

The compounds and their decomposition products were identified by matching the background-subtracted mass spectra of GC peaks with a forward library search of the NBS mass spectral library of 39,763 compounds.

A cold, on-column injection technique was evaluated for the organophosphorous compounds using the following conditions:

GC:	- Carlo Erba Model 4160, equipped with on-column injector
GC Column:	- DB-1 wide bore fused silica capillary 30 m x 0.32 mm ID with a 0.25 µm film thickness
Column Temperature Program:	- 35°C to 300°C at 8°C/min
Carrier:	- H_2 at 50 cm/sec room temperature
Detector Temperature:	- 300°C
Injection Volume:	- 1 µL on-column

Extraction Studies

The extraction efficiency of trichlorfon from water using standard separatory funnel techniques was evaluated at neutral pH with methylene chloride as the extraction solvent.

Five replicate samples were prepared at a 100 µg/L spike level by the addition of 100 µL of a 1.0 mg/mL stock solution of the compounds (in methanol) to each of five 1-L aliquots of reagent water. Prior to spiking, the reagent water was buffered at pH 7.0 with 1.0 mM phosphate buffer. The samples and one reagent blank were extracted with methylene chloride, dried with sodium sulfate, and concentrated using KD techniques to approximately 10 mL. At this time 100 µg of phenanthrene was added as an internal standard (IS), and the samples concentrated to 1 mL after exchange to hexane. Addition of internal standard prior to final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained. The samples were then analyzed by GC using the chromatographic system and conditions described for the SPB-5 column in Table 2.

A reverse phase cartridge extraction technique was evaluated for recovery of mevinphos and trichlorfon by spiking three 50 mL replicates of reagent water (pH 4.5 with pH paper) with 100 µg of each compound from a 1000 µg/mL methanol stock solution and passing the spiked water sample through cleaned reverse phase cartridges (Baker 6-mL C_{18} cartridges) using the Baker-10 Solid Phase Extraction System. The cleanup procedure was 10 mL of hexane followed by 10 mL of methanol, with a 50-mL reagent water equilibration rinse. The cartridges were eluted after adsorption of the spiked water samples with 5.0 mL of methanol followed by 5.0 mL of hexane. After collection of the eluates, 20 µg of phenanthrene (IS) were added and the eluates concentrated by KD techniques to 1 mL for GC analysis using on-column injection and conditions (described previously). Addition of the internal standard prior to final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained.

Evaluation of Kuderna-Danish Concentration Recovery

In addition to the extraction experiments, the recovery of mevinphos and trichlorfon during KD concentration was evaluated. Three replicate samples containing 100 µg each of the two compounds and 20 ug

of phenanthrene (IS) in 180 mL of methylene chloride, plus one process blank were concentrated to 1 mL for GC analysis using on-column injection as described previously. This experiment was repeated using 180 mL of methyl t-butyl ether (two replicates and one blank). Finally, a third experiment was performed in which 100 µg each of mevinphos and trichlorfon were placed in a KD tube with 5 mL of hexane, 5 mL of methanol, and 0.1 mL of reagent water. Twenty µg of phenanthrene (IS) were added, and the solutions concentrated by KD distillation to 1 mL (two replicates and one solvent blank). Addition of the internal standard prior to concentration is a deviation from standard EPA methodology, but it is not significant in this case.

RESULTS AND DISCUSSION

Literature Review

A report (2) provided by EMSL-Cincinnati on the semivolatile high-interest compounds was reviewed to determine what problems had occurred on previous attempts to develop analytical methods for these compounds. This report indicates that trichlorfon is not extracted from water using EPA Method 625 procedures, and that mevinphos and trichlorfon elute at 21:42 and 3:09 minutes, respectively, using EPA Method 625 chromatographic conditions. These retention time data are inconsistent with those generated in this study which are presented in a later section and show that trichlorfon elutes very near mevinphos. The peak identified as trichlorfon in the referenced report was probably a decomposition product produced in the injection port of the gas chromatograph, transfer lines, or metal bulkheads of the mass spectrometer.

Chromatographic Separations

The elution order and precision of retention time for eight of the 12 organophosphorous compounds on the SPB-5 column is presented in Table 3. Of the eight compounds evaluated, seven were detected chromatographically and one compound, trichlorfon, did not show any response

TABLE 3. PRECISION OF RETENTION TIME FOR ORGANOPHOSPHOROUS COMPOUNDS ON SPB-5 FUSED SILICA CAPILLARY COLUMN

Compound	Retention Time for Given Replicate, min			Average	SD(a)	RSD%(b)
	Rep 1	Rep 2	Rep 3			
Mevinphos	15.11	15.11	15.11	15.11	0.00	0.00
Diazinon	20.91	29.92	29.92	29.92	0.0058	0.03
Disulfoton	21.01	21.01	21.01	21.01	0.00	0.00
Methyl parathion	22.17	22.17	22.18	22.17	0.0058	0.03
Malathion	23.20	23.21	23.21	23.21	0.0058	0.02
Parathion	23.49	23.49	23.50	23.49	0.0058	0.02
Guthion	29.90	29.91	29.91	29.91	0.0058	0.02
Trichlorfon	NC(c)	NC	NC	NA(d)	NA	NA

(a) SD = standard deviation.
(b) RSD = percent relative standard deviation.
(c) NC = component did not chromatograph under specified conditions.
(d) NA = not applicable.

on the FID detector, presumably due to decomposition. This compound is reportedly decomposed by heat to form chloral hydrate and trichloroethanol (3) and by water at high temperature to form dichlorvos (4). Analysis of trichlorfon using an injector temperature of 200°C also failed to give a significant GC peak attributable to the subject analyte. Another compound similar in structure to trichlorfon, mevinphos, was found to give a low response at concentrations equivalent to the other compounds shown in Table 3, which could possibly indicate partial decomposition of this compound. The problem of analyte decomposition in the injector is addressed separately, below. A chromatogram showing the separation of seven of the eight organophosphorous compounds evaluated is presented in Figure 1, and the region of this chromatogram from 20 to 25 minutes elution time is shown expanded in Figure 2. The elution order for all compounds in this class is presented in Table 4. Of the 12 organophosphorous compounds, only parathion and chlorpyrifos were found to coelute. However, diazinon and disulfoton are only partially separated, and malathion elutes very close to the parathion/chlorpyrifos coelution pair. A chromatogram showing the separation of this class of compounds on the SPB-5 column is presented below in the section under injection conditions. Elution orders for these compounds were verified using GC/MS with equivalent chromatographic conditions.

The chromatography for this class was also evaluated on the Carbowax 20M fused silica column, but only two compounds were found to elute. Presumably these compounds were mevinphos and trichlorfon, although the components eluting could have been decomposition products of other noneluting compounds of the class. This column was not evaluated further for this class of compounds.

Evaluation of Injection Conditions

Chromatograms obtained using split injection showing the appearance of decomposition products and loss of trichlorfon and naled with increasing injector temperature are presented in Figures 3, 4, and 5 for injector temperatures of 200, 250, and 300°C, respectively. In Figure 3, with injection at 200°C, all components are present in the

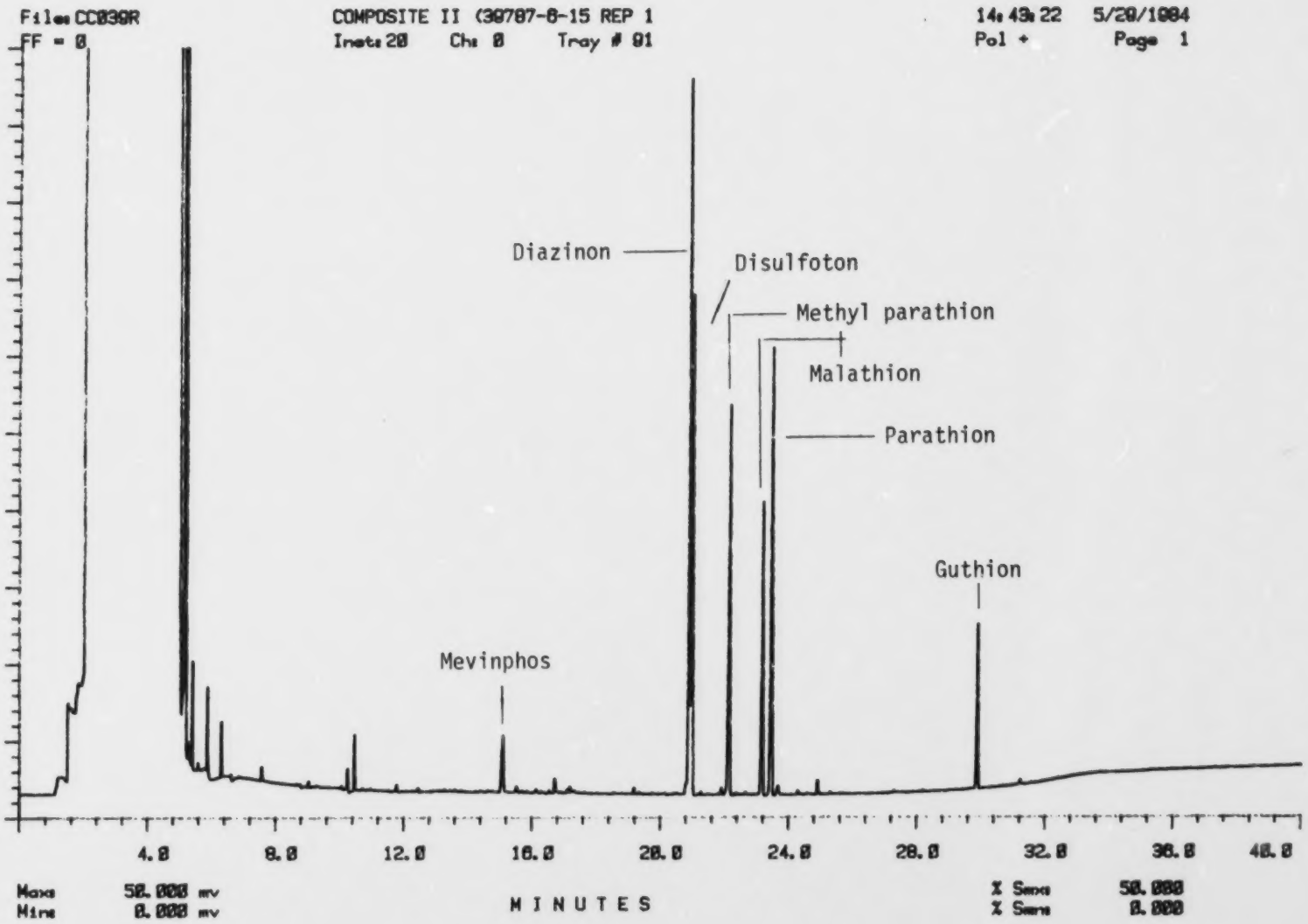

Figure 1. GC-FID chromatogram of organophosphorous compounds.

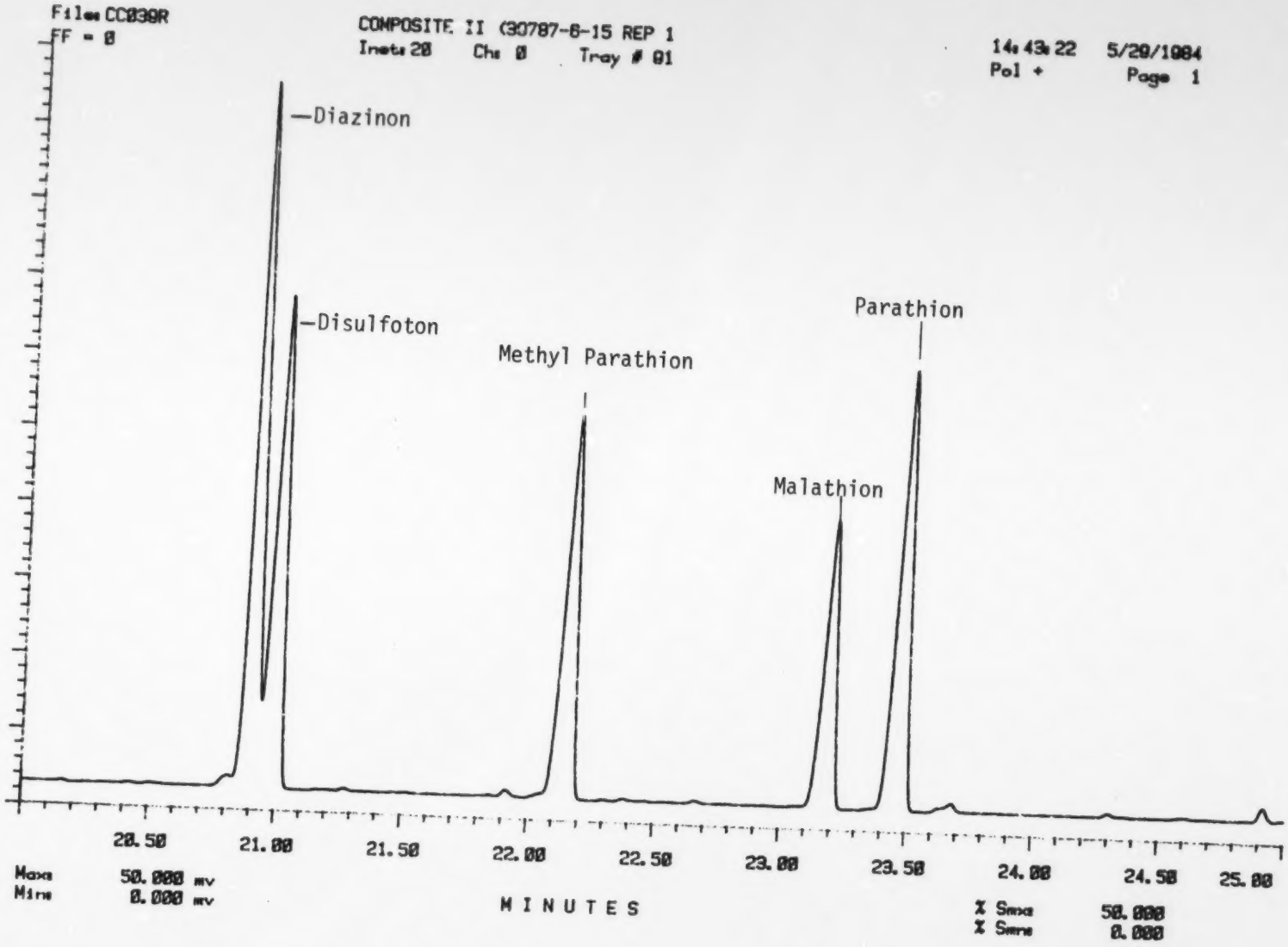

Figure 2. Expanded GC-FID chromatogram of organophosphorous compounds.

TABLE 4. RETENTION TIMES OF ORGANOPHOSPHOROUS COMPOUNDS ON SPB-5 FUSED SILICA CAPILLARY COLUMN

Compound	Retention Time, min[a]
Mevinphos	15.2
Trichlorfon	15.6
Naled	18.8
Diazinon	21.0
Disulfoton	21.1
Methyl parathion	22.2
Malathion	23.3
Chloropyrifos	23.6[b]
Parathion	23.6[b]
Ethion	27.1
Guthion	30.2
Coumaphos	31.7

(a) Elution times may vary slightly from those presented in Table 3.
(b) These compounds coelute.

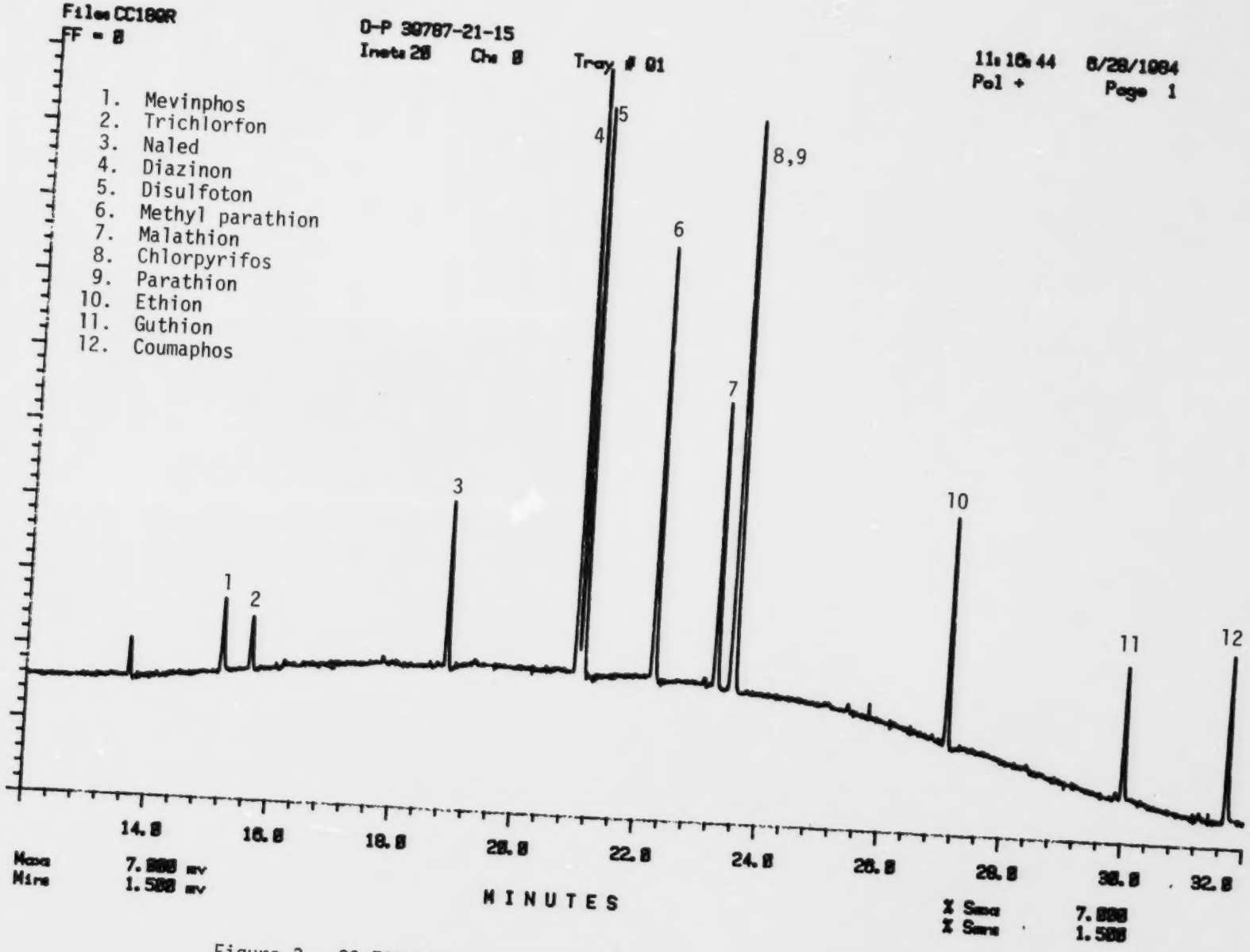

Figure 3. GC-FID chromatogram of the organophosphorous compounds analyzed with a 200°C injector temperature.

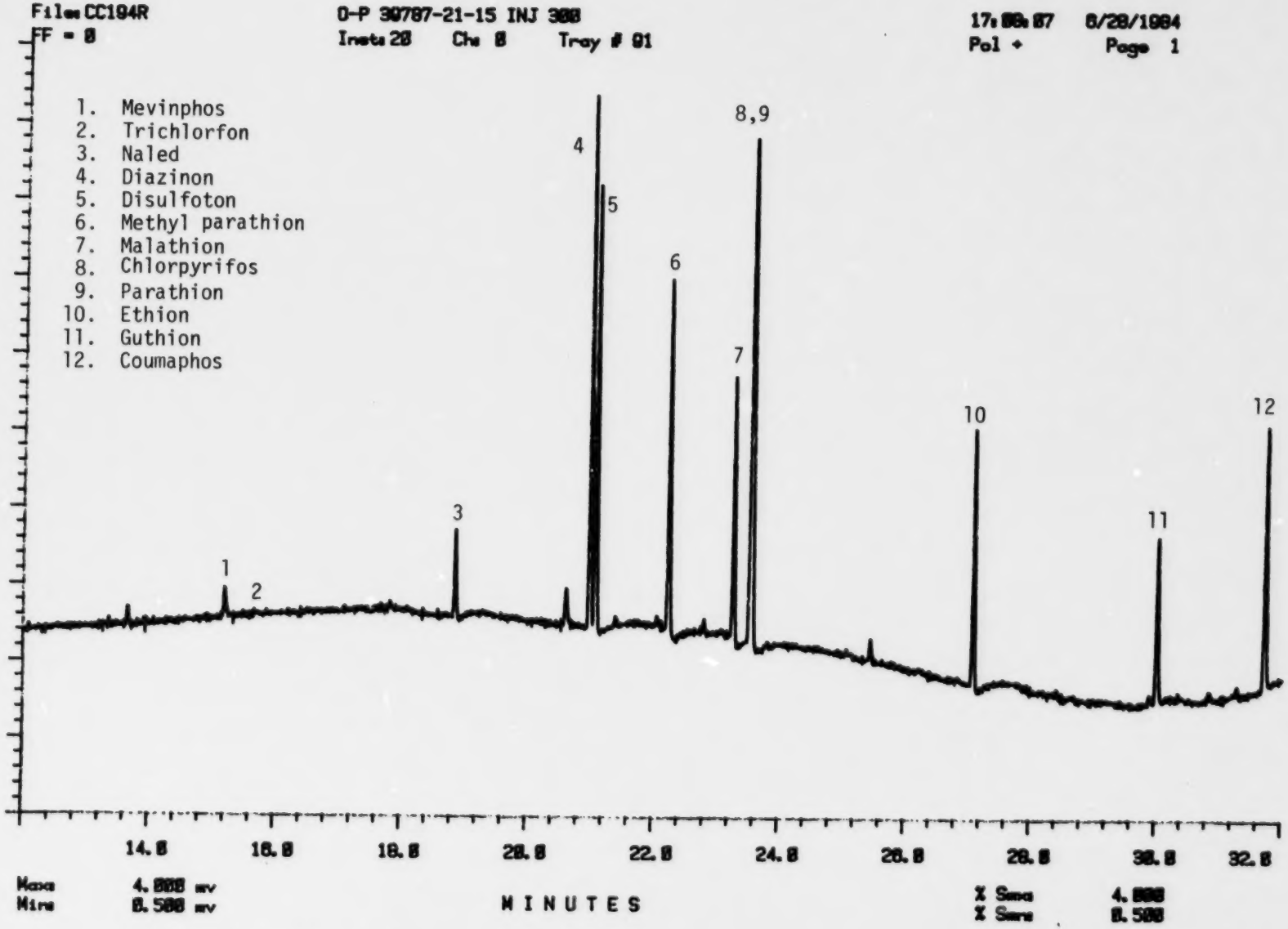

Figure 4. GC-FID chromatogram of the organophosphorous compounds analyzed with a 250°C injector temperature.

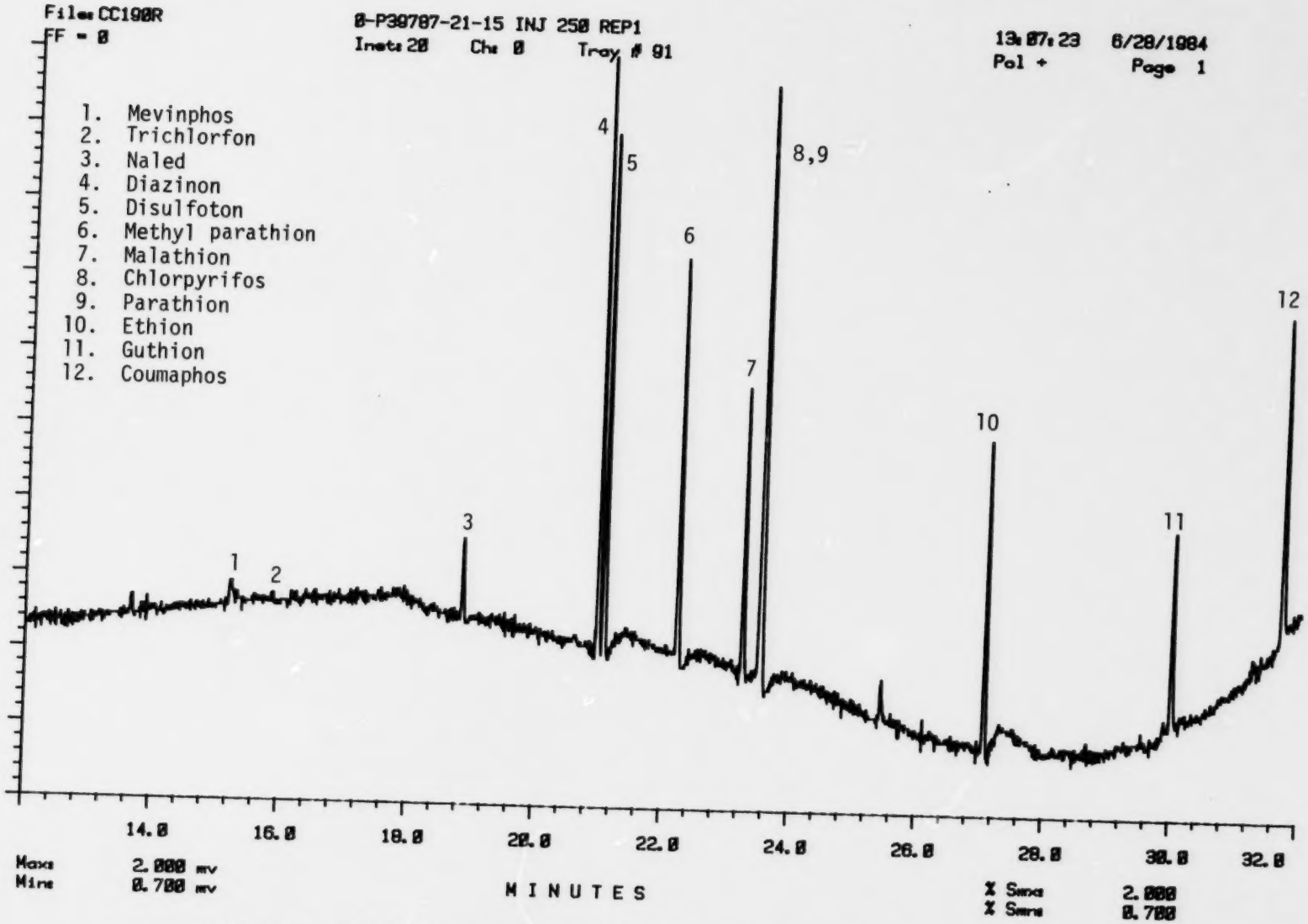

Figure 5. GC-FID chromatogram of the organophosphorous compounds analyzed with a 300°C injector temperature.

chromatogram, although the response for mevinphos and trichlorfon are quite low compared to the other components. In Figure 4, with injection at 250°C, the response for mevinphos and naled are reduced when compared to the other components, and trichlorfon is absent from the chromatogram. In Figure 5, with injection at 300°C, the same effect is observed as for the 250°C injection, but in addition, there appear to be some additional peaks in the chromatogram which may be decomposition products of other organophosphorous compounds. These data indicate that the maximum injector temperature for these compounds should be 200°C if one is interested in determining trichlorfon along with the other organophosphorous compounds. The trichlorfon peak was confirmed to be the parent and not a decomposition product molecule by GC/MS, and the identities of the other major peaks were confirmed as shown in Figures 4 and 5.

The organophosphorous compounds were analyzed using an on-column injection technique to evaluate the differences in response for trichlorfon, and a chromatogram showing the response differences is presented in Figure 6. In this chromatogram, trichlorfon (peak 2) has approximately twice the response of mevinphos (peak 1), whereas, with standard injection at 200°C (Figure 3), the trichlorfon peak is smaller. These data suggest that at 200°C injection, only about half of the trichlorfon is present as the parent substance. Peak shapes are poor due to peak splitting for all compounds using the on-column technique, but this effect could be eliminated with the use of a retention gap of fused silica and/or modification of the injection amount and column oven temperature at injection. All subsequent work with trichlorfon employed cold, on-column injection.

Extraction Studies

Trichlorfon was not recovered at neutral pH using methylene chloride and the standard separatory funnel extraction techniques. The high polarity of the compound probably makes it difficult to extract, although decomposition in aqueous solution is the more likely explanation for the low recoveries.

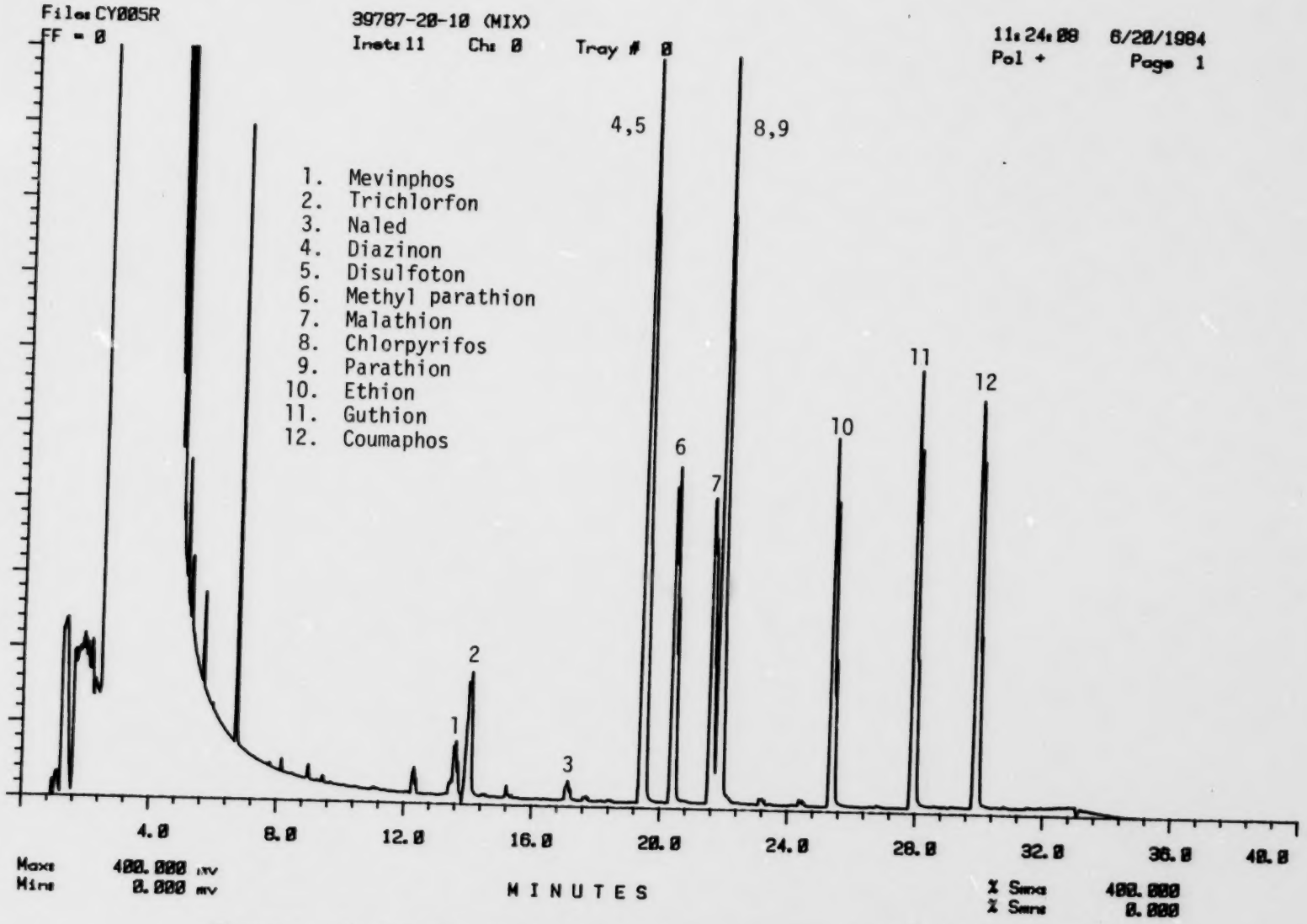

Figure 6. GC-FID chromatogram of the organophosphorous compounds obtained using on-column injection at 35°C.

The results of the reverse phase cartridge extraction of trichlorfon and mevinphos were inconclusive due to the lack of recovery of trichlorfon and the very low recovery in the methanol fraction (3 to 5 percent) for mevinphos. These results suggested that either the compounds were not extracted efficiently or that the two analytes were decomposing during the KD concentration step.

Evaluation of Kuderna-Danish Concentration Recovery

The results of the KD concentration experiment for mevinphos and trichlorfon dissolved in methylene chloride are presented in Table 5, and the results of the KD concentration experiment for these compounds dissolved in methyl t-butyl ether are presented in Table 6.

TABLE 5. RECOVERY OF MEVINPHOS AND TRICHLORFON AFTER KUDERNA-DANISH CONCENTRATION IN METHYLENE CHLORIDE

Compound	Amount Spiked, µg	Amount Found in Given Replicate, µg						Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Average	SD	RSD%	
Mevinphos	100	120.0	88.6	92.0	100	17	17	100
Trichlorfon	100	108.0	70.6	70.8	83	21	25	83

TABLE 6. RECOVERY OF MEVINPHOS AND TRICHLORFON AFTER KUDERNA-DANISH CONCENTRATION IN METHYL T-BUTYL ETHER

Compound	Amount Spiked, µg	Amount Found in Given Replicate, µg			Average Percent Recovery
		Rep 1	Rep 2	Average	
Mevinphos	100	97.0	99.8	98	98
Trichlorfon	100	104.0	104.7	104	104

These data indicate that KD concentration in methylene chloride or methyl t-butyl ether is not responsible for the decomposition of trichlorfon or mevinphos and suggest that the reason for low recovery using the solvent extraction techniques described above is due to decomposition of the analytes in aqueous solution or low extraction efficiency.

To further define the source of losses in the reverse phase extraction procedure, a KD concentration experiment was performed using 50/50 (v/v) methanol/hexane. The results are presented in Table 7.

TABLE 7. RECOVERY OF MEVINPHOS AND TRICHLORFON AFTER KUDERNA-DANISH CONCENTRATION IN 50/50 (V/V) METHANOL/HEXANE

Compound	Amount Spiked, µg	Amount Found in Given Replicate, µg			Average Percent Recovery
		Rep 1	Rep 2	Average	
Mevinphos	100	80.6	91.2	85	85
Trichlorfon	100	20.6	28.5	24	24
Dichlorvos(a)	0	29.8	28.8	29	--(b)

(a) Decomposition product of trichlorfon.
(b) Recovery not applicable since dichlorvos is a decomposition product of trichlorfon.

The results shown in Table 7 indicate that mevinphos does not decompose significantly during KD concentration, and that the inability to recover mevinphos using the reverse phase extraction technique is due to either decomposition of mevinphos in aqueous solution or poor extraction desorption efficiency. These reverse phase cartridge extraction results indicate that decomposition of mevinphos in aqueous media is the more probable explanation. Since 3 to 5 percent of mevinphos was recovered in the methanol eluate after reverse phase extraction, the remaining 97 to 95 percent would still be in the water

if decomposition were not taking place. However, re-extraction of such a cartridge extracted spiked water sample yielded no mevinphos in the methanol eluates. Thus, these results suggest that this compound decomposes in water. However, decomposition of mevinphos in water is reported to be relatively slow with half lines of 1.4 hr (pH 11), 3 days (pH 9) and 35 days (pH 7) (4). For the present, the cause of low extraction efficiency for mevinphos must remain unknown.

The trichlorfon results from the KD experiment with methanol/hexane indicate poor recovery due to decomposition and rearrangement to dichlorvos during the concentration. These results indicate that KD concentration in a polar solvent such as methanol, which is required for reverse phase cartridge elution, is unsuitable due to trichlorfon decomposition.

Further experimentation with the organophosphorous compounds was not performed due to the inability to recover trichlorfon from aqueous samples.

CONCLUSIONS

Trichlorfon was not stable in water under any conditions, and therefore may not be of concern as a waterborne pollutant. I.. addtion, cold, on-column injection is required for fused silica capillary GC analysis of this compound.

RECOMMENDATIONS

A detailed study of the kinetics of trichlorfon decomposition in water is required before the need for further analytical work can be justified.

SECTION 5

NEUTRAL NITROGEN COMPOUNDS

Benzonitrile is the only neutral nitrogen compound of the high-interest chemicals (Table 1). The following additional neutral nitrogen compounds listed in Appendix D to 40 CRF 144 were evaluated with benzonitrile:

Carbaryl	Diuron
Carbofuran	Methiocarb
Dichlobenil	Mexacarbate
1,2-Dinitrobenzene	2-Nitrotoluene
1,3-Dinitrobenzene	3-Nitrotoluene
1,4-Dinitrobenzene	4-Nitrotoluene

EXPERIMENTAL

Chromatographic Separations

All chromatographic evaluations were performed on the Hewlett-Packard 5730 gas chromatograph using the SPB-5 and Carbowax 20 M fused capillary columns and instrumental operating conditions described in Table 2. Target compound and decomposition products were verified by GC/MS using DB-5 fused silica capillary column, equivalent to the SPB-5 column used for GC separations. Analytes were injected singly and as mixtures in appropriate injection solvents, generally at 50 µg/mL.

Evaluation of Injection Conditions

Standard heated evaporator cavity injections were made at 200, 250, and 300°C as described above under organophosphorous compounds to evaluate the effect of injector temperature on compound stability. These studies were performed on the HP-5730 GC using the SPB-5 fused capillary column and conditions described in Table 2.

Extraction Studies

The efficiency of removing benzonitrile from water by separatory funnel extraction with methylene chloride was evaluated. Replicate spiked samples were prepared by dissolving 100 µg of benzonitrile into each of five 1-L aliquots of reagent water. Prior to spiking, the water had been buffered at pH 7.0 with 1.0 mM phosphate buffer. The five spiked samples and one reagent blank were extracted separately with three 60-mL portions of methylene chloride, dried with sodium sulfate, and concentrated by KD procedures to 1.0 mL. The concentrated extracts were analyzed by gas chromatography using the conditions described above.

Evaluation of Column Cleanup Technique

A Florisil cleanup procedure was evaluated for elution patterns and recovery of selected neutral nitrogen compounds. These compounds included benzonitrile, 2-, 3-, and 4-nitrotoluene, dichlobenil, 1,2-, 1,3-, and 1,4-dinitrobenzene, carbaryl, mexacarbate, methiocarb, and carbofuran. Each of the above compounds (100 µg) was placed in 10 mL of hexane and placed at the top of a Chromaflex column containing 20 g of Florisil in hexane. Prior to use, the column had been activated at 130°C overnight. The column was serially eluted with the following elution solvents:

Fraction 1: 200 mL of 20% ethyl ether in hexane
Fraction 2: 200 mL of 6% acetone in hexane
Fraction 3: 200 mL of 15% acetone in hexane
Fraction 4: 200 mL of 50% acetone in hexane.

The fractions were collected separately, 20 µg of phenanthrene (IS) added, and the fractions concentrated to 1 mL for GC analysis (described previously). Addition of the internal standard prior to final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained.

Evaluation of Method Precision and Accuracy

The precision and accuracy for the determination of the neutral nitrogen compounds was evaluated by combining the methylene chloride extraction and Florisil cleanup procedures with the fused silica capillary column separation developed under this program (described above) and a nitrogen phosphorous detector (NPD).

Four 1-L replicates of reagent water were spiked with 25 µg each of benzonitrile, 2-, 3-, and 4-nitrotoluene, dichlobenil, 1,2-, 1,3-, and 1,4-dinitrobenzene, carbofuran, mexacarbate, carbaryl, and methiocarb. The samples were extracted serially with three 60-mL aliquots of methylene chloride, which were combined, dried with sodium sulfate, and concentrated to approximately 5 mL using KD apparatus. Sample extracts were exchanged to hexane and taken through the Florisil cleanup procedure. The appropriate Florisil eluates were combined, concentrated to 2.0 mL, and analyzed by GC-NPD using the following conditions:

Column Temperature Program:	55°C (2 min hold); 8°C/min to 330°C (2 min hold)
Injection Volume:	2 µL splitless
Detector:	NPD
Injector Temperature:	300°C

RESULTS AND DISCUSSION

Chromatographic Separations

The retention times and elution order for the thirteen neutral nitrogen compounds on the SPB-5 column and the Carbowax 20M fused silica capillary columns are presented in Table 8. Of the thirteen compounds, only diuron did not elute as the parent compound under the conditions used. The observed peak for diuron appears to be an isocyanate derivative produced on injection, as determined by GC/MS analysis (described below). A chromatogram showing the separation of the neutral nitrogen compounds on the SPB-5 column is presented below in the section on injection conditions.

TABLE 8. RETENTION TIMES OF NEUTRAL NITROGEN COMPOUNDS ON FUSED SILICA CAPILLARY COLUMNS

Compound	Retention Time on Given Column, min	
	SPB-5	Carbowax 20 M
Benzonitrile	5.9	11.6
2-Nitrotoluene	9.9	14.4
3-Nitrotoluene	10.7	15.1
4-Nitrotoluene	11.0	15.6
Diuron	12.7	23
Dichlobenil	13.6	19.4
1,4-Dinitrobenzene	15.1	--(a)
1,3-Dinitrobenzene	15.5	--
1,2-Dinitrobenzene	15.9	24.7
Carbofuran	20.2	20.0(b)
Mexacarbate	21.3	23.0(b)
Carbaryl	22.4	28.7(b)
Methiocarb	23.0	27.2(b)

(a) Dash indicates compound did not elute from the column.
(b) These peaks are probably decomposition products rather than the actual components since injection was at 250°C.

Evaluation of Injection Conditions

Chromatograms showing the appearance of decomposition products of the neutral nitrogen compounds with increasing injector temperatures are presented in Figures 7, 8, and 9 for injector temperatures of 200, 250 and 300°C, respectively. In Figure 7, all compounds except diuron, are shown separated, with good chromatographic peak shapes. Peak identities were confirmed by GC/MS. Only small amounts of decomposition products are observed. However, as the injection port temperature is increased from 200°C to 250°C, and finally to 300°C, the decomposition products of the four carbamates become more pronounced. These decomposition products were confirmed by GC/MS, and are listed in Table 9. One component of the neutral nitrogen mixture, 1,4-dinitrobenzene, is present at a 10-fold lower concentration than the other compounds, and hence shows a lower response in the chromatograms of Figures 7, 8 and 9.

Extraction Studies

Benzonitrile recoveries ranged from 90.4 to 111 percent, with an average of 103 and a standard deviation of 8.0 percent. These data indicate that recovery of benzonitrile from water is quantitative when using methylene chloride as an extraction solvent. No further work was conducted on extractability of this compound. Extractibilities of the other compounds in this class were not evaluated, since these compounds are already listed in EPA wastewater methods.

Evaluation of Column Cleanup Technique

The results of the Florisil cleanup experiment are presented in Table 10. These data show recoveries of 79 percent or greater for all compounds except mexacarbate (38 percent) and methiocarb (34 percent). The majority of the compounds elute in the 6 percent acetone in hexane fraction.

Evaluation of Method Precision and Accuracy

The results of the method precision and accuracy determinations for the neutral nitrogen compounds are presented in Table 11. Recoveries

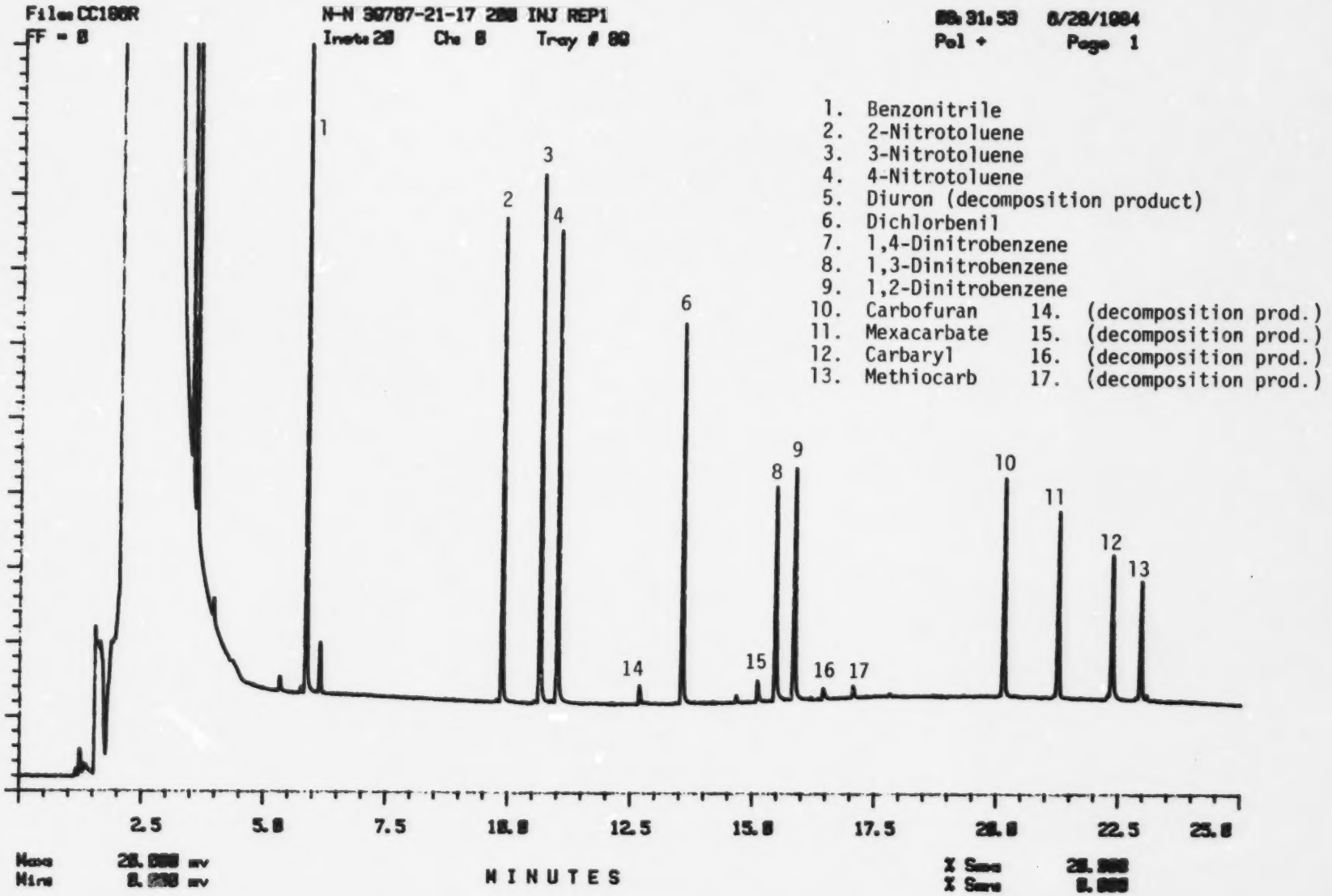

Figure 7. GC-FID chromatogram of neutral nitrogen compounds analyzed with a 200°C injector temperature.

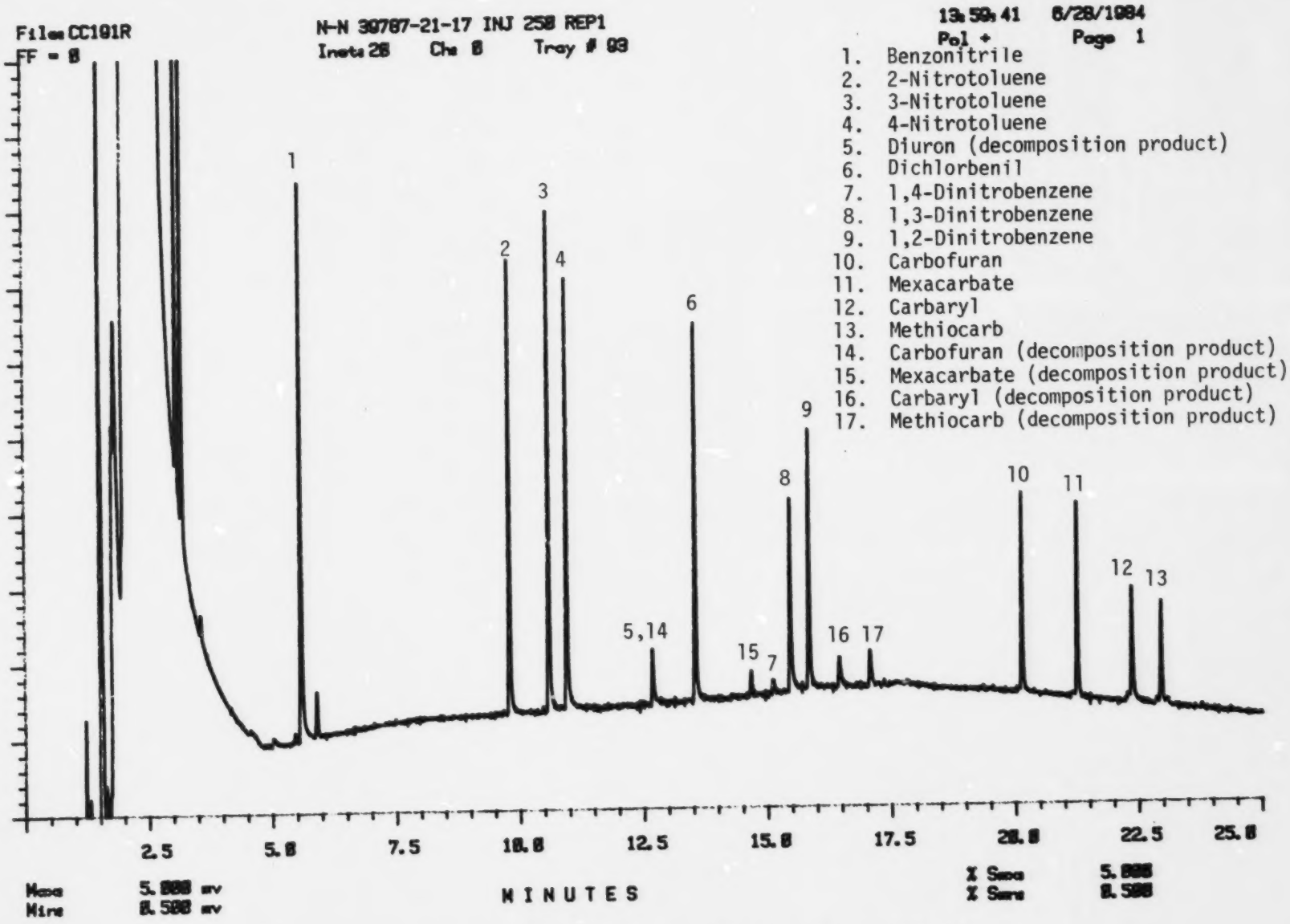

Figure 8. GC-FID chromatogram of neutral nitrogen compounds analyzed with a 250°C injector temperature.

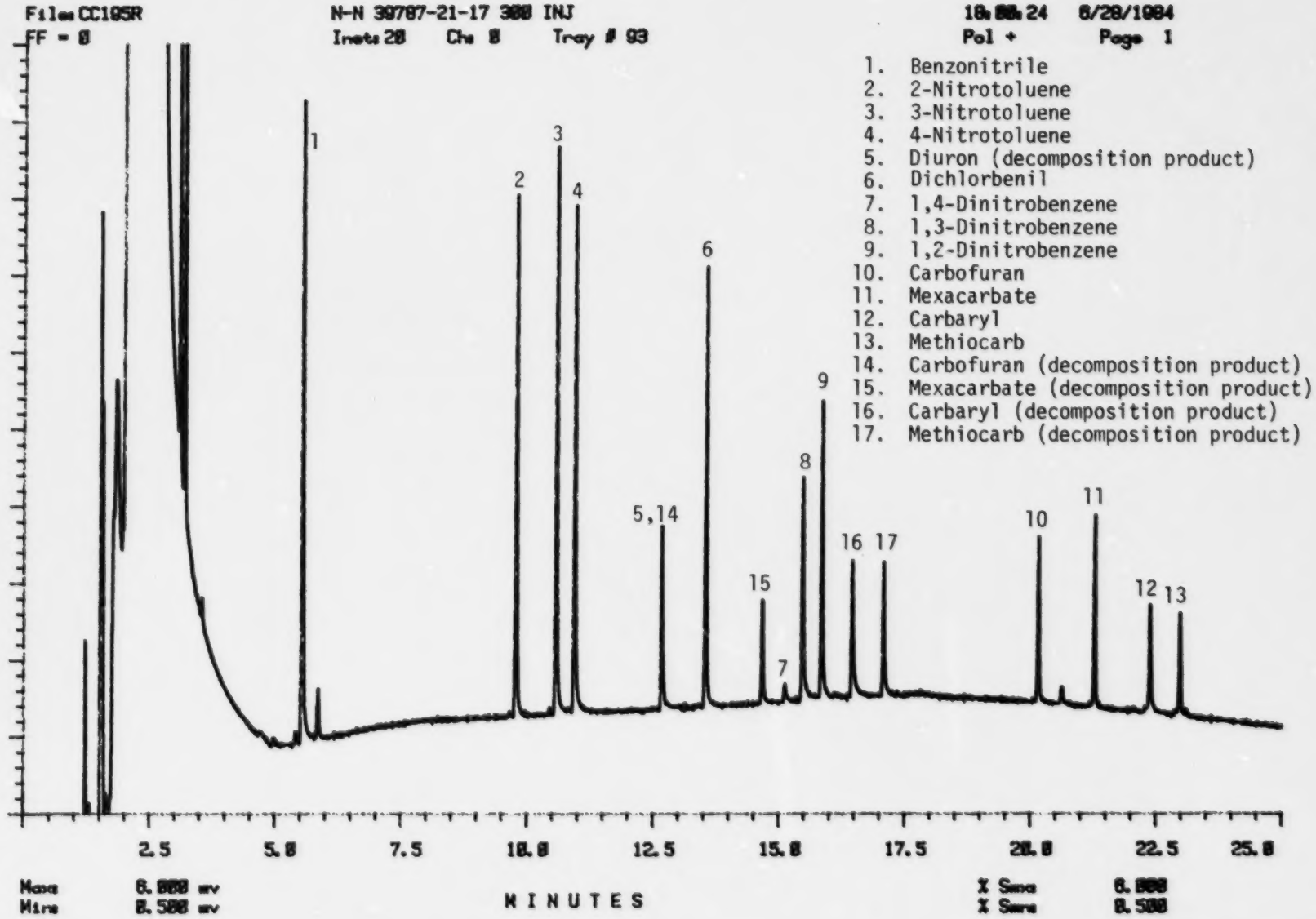

Figure 9. GC-FID chromatogram of neutral nitrogen compounds analyzed with a 300°C injector temperature.

Table 9. SUMMARY OF DECOMPOSITION PRODUCTS OF NEUTRAL NITROGEN COMPOUNDS

Retention Time, min	Parent Compound	Decomposition Product
12.7(a)	Diuron	3,4-Dichloro-2-isocyanato benzene ($C_7H_3ONCl_2$)
12.7(a)	Carbofuran	2,3-Dihydro-2,2-dimethyl-7-benzofuranol ($C_{10}H_{12}O_2$)
14.7(b)	Mexacarbate	3,5-Dimethyl-4-(dimethylamino) phenol ($C_{10}H_{15}OH$)
16.5	Carbaryl	1-Hydroxynaphthalene ($C_{10}H_8O$)
17.1	Methiocarb	3,5-Dimethyl-4-(methylthio)-phenol ($C_{11}H_{15}O_2NS$)

(a) These decomposition products coelute on the SPB-5 column, but are separated on the DB-5 column used for GC/MS analysis.
(b) This product not confirmed by GC/MS since mexacarbate was not available at the time the determinations were made.

TABLE 10. RECOVERY OF NEUTRAL NITROGEN COMPOUNDS FROM FLORISIL CLEANUP PROCEDURE

Compound	Amount Spiked, µg	Amount Found in Given Fraction, µg: 20% Diethyl Ether in Hexane Rep 1	Rep 2	Rep 3	6% Acetone in Hexane Rep 1	Rep 2	Rep 3	15% Acetone in Hexane Rep 1	Rep 2	Rep 3	50% Acetone in Hexane Rep 1	Rep 2	Rep 3	Average Total Recovery	SD	RSD%	Average Percent Recovery
Benzonitrile	107	1.3	1.0	0.7	88	78	87	--	(a)--	--	--	--	--	85	5.5	6.5	79
2-Nitrotoluene	103	85	86	94	14	9.7	4.1	--	--	--	--	--	--	98	1.7	1.2	95
3-Nitrotoluene	106	75	79	90	27	18	10	--	--	--	--	--	--	100	2.5	2.5	94
4-Nitrotoluene	108	35	43	60	68	52	41	--	--	--	--	--	--	100	4.2	4.2	92
Dichlorbenil	119	0.3	1.2	5.6	104	97	98	--	--	--	--	--	--	102	3.3	3.3	86
1,3-Dinitrobenzene(c)	100	--	--	--	100	99	101	--	--	--	--	--	--	100	1.0	1.0	100
1,2-Dinitrobenzene(c)	108	--	--	--	98	95	98	3.9	4.0	4.4	--	--	--	101	1.8	1.8	94
Carbofuran	108	--	--	--	0.7	4.3	7.4	123	126	128	--	--	--	130	5.9	4.5	120
Mexacarbate	103	--	--	--	34	38	37	2.1	3.2	2.7	--	--	--	39	2.6	6.7	38
Carbaryl	108	--	--	--	--	1.2	2.0	94	96	106	--	--	--	100	7.3	7.3	93
Methiocarb	111	--	--	--	29	37	44	1.0	1.6	2.4	--	--	--	38(b)	8.2	21	34

(a) Dash (-) indicates compound was not recovered in given replicate.

(b) Chromatographic interference problem (severe peak tailing) affects integration.

(c) 1,4-Dinitrobenzene was inadvertantly spiked at too low a level for meaningful quantitative results and has therefore been omitted.

TABLE 11. PRECISION AND ACCURACY OF NEUTRAL NITROGEN COMPOUND DETERMINATIONS

Compound	Spike Level, µg/L	Amount Found in Given Replicate, µg/L				Average	SD	RSD%	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4				
Benzonitrile	25	20	19	18	16	18	1.7	9.4	72
2-Nitro-toluene	25	23	21	19	17	20	2.6	13	80
3-Nitro-toluene	25	23	21	19	17	20	2.6	13	80
4-Nitro-toluene	25	24	21	19	16	20	3.4	17	80
Dichlobenil	25	24	21	19	17	20	3.0	15	80
1,4-Dinitro-benzene	25	26	17	15	13	18	5.7	32	72
1,3-Dinitro-benzene	25	19	18	16	12	16	3.1	19	64
1,2-Dinitro-benzene	25	20	19	17	14	18	2.6	15	72
Carbo-furan	25	48	33	22	16	30	14	47	120
Mexacar-bate	25	--(a)	--	31	18	24	--	--	98
Carbaryl	25	55	32	36	21	36	14	39	144
Methio-carb	25	1.5	0.29	3.8	4.2	2.4	1.9	76	10

(a) Dash indicates compound not detected

and precisions for benzonitrile, the three nitrotoluenes and three nitrobenzenes, and dichlobenil are reasonable, with the possible exception of 1,4-dinitrobenzene, which showed a precision of greater than 30 percent RSD for four replicates. The interpretation of data for carbofuran, mexacarbate, carbaryl, and methiocarb is unclear.

Replicates 3 and 4 were analyzed within one week of extraction and cleanup. At that time, drifting detector response prevented the completion of the data set. These results were presented because the samples were analyzed either immediately before or immediately after a calibration standard of a similar level. Methiocarb was not found in the sample extracts. Since this compound was present in the calibration standards and the same stock solution was used for the preparation of both spiked waters and calibration standards, it follows that the compound either decomposed or was not extracted from the water. The results for replicates 1 and 2 for mexacarbate indicate that this compound decomposed in the extract between the time it was first analyzed (replicates 3 and 4) and the second set of analyses, a period of approximately four weeks. Carbofuran and carbaryl gave extremely high results for the reanalysis (replicates 1 and 2 presented in Table 11), indicating a possible interference problem. The data for the carbamate pesticides indicate some stability problems in the organic extract that have not been evaluated.

CONCLUSIONS

Benzonitrile can be effectively determined using methylene chloride extraction, Florisil column cleanup, and fused silica capillary column GC analysis. Somewhat erratic results for carbofuran, mexacarbate, carbaryl and methiocarb prevent making any definative method performance conclusions. The overall recoveries obtained for the nitrotoluenes, dinitrobenzenes and dichlobenil were generally acceptable at 70 to 80 percent (except 1,3-dinitrobenzene at 64 percent) with RSD% values of about 15 percent (except 1,4- and 1,3-dinitrobenzene).

RECOMMENDATIONS

Benzonitrile can be included in EPA Method 633 without modification other than the use of fused silica capillary chromatography.

SECTION 6

CHLORINATED PESTICIDES

The high-interest compounds from Table 1 evaluated under this group included dichlone and kepone. Methoxychlor and captan from Appendix D to 40 CFR 122 were also included in this evaluation. While kepone is not chlorinated, it was considered to have chemical characteristics which would make it amenable to analysis methods used for dichlone, captan, and methoxychlor which are chlorinated pesticides. For simplicity, all four compounds are referred to as chlorinated pesticides in this report.

EXPERIMENTAL

Chromatographic Separations

The separation of captan, dichlone, kepone, and methoxychlor was evaluated on both the SPB-5 and Carbowax 20M fused silica capillary columns using the instrumentation and conditions listed in Table 2. An evaluation of injection conditions was not undertaken for this class of compounds. Analytes were injected singly and in mixtures in appropriate injection solvents, generally at 50 µg/mL.

Extraction Studies

The extraction efficiency from water of the chlorinated pesticides was evaluated at neutral pH with methylene chloride as the extraction solvent. Five replicates were prepared at the 100 µg/L spike level in reagent water by the addition of 100 µL of a 1.0 mg/mL stock solution of the compounds (in methanol). Prior to spiking, the reagent water was buffered at pH 7.0 with 1.0 mM phosphate buffer. The samples and one reagent blank were extracted with methylene chloride, dried with sodium sulfate, and concentrated using KD techniques to approximately 10 mL.

At this time 100 µg of phenanthrene (IS) were added, and the samples concentrated to 1 mL after exchange to hexane. Addition of internal standard prior to final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained. Samples were analyzed by GC with the SPB-5 column using the Table 2 instrumentation and conditions.

Evaluation of Column Cleanup Techniques

A Florisil cleanup procedure was evaluated for elution patterns and recovery of dichlone, kepone, methoxychlor, and captan. These compounds (100 µg of each in 10 mL of hexane) were placed at the top of a Chromaflex column containing 20 g of Florisil (activated at 130°C overnight) and serially eluted with the following elution solvents:

Fraction 1: 200 mL of 6% ethyl ether in hexane
Fraction 2: 200 mL of 15% ethyl ether in hexane
Fraction 3: 200 mL of 50% ethyl ether in hexane.

The fractions were collected separately, 20 µg of phenanthrene (IS) were added, and the fractions were concentrated to 1 mL and exchanged to hexane for GC analysis (described above).

A second experiment was performed in which 100 µg each of dichlone, captan and kepone were placed on a 20 g Florisil column and serially eluted with the following fractions:

Fraction 1: 200 mL of 50% ethyl ether in hexane
Fraction 2: 200 mL of ethyl ether
Fraction 3: 200 mL of 5% acetone in ethyl ether.

The fractions were collected separately, 20 µg of phenanthrene (IS) were added, and the fractions were concentrated to 1 mL and exchanged to hexane for GC analysis (described previously). Addition of internal standard prior to final concentration in these two experiments is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained.

Evaluation of Kuderna-Danish Concentration Recovery

Prior to the evaluation of the second elution scheme (above) for chlorinated pesticides, the recovery of the compounds during KD concentration was studied. Three 100 µg aliquots of each of the four chlorinated pesticides were placed in 180 mL of 15% ethyl ether in hexane and concentrated to 1.0 mL for GC analysis (described previously).

Evaluation of Method Accuracy and Precision

The method precision and accuracy for the determination of the chlorinated pesticides were evaluated by combining methylene chloride extraction with a Florisil cleanup procedure and using fused silica capillary column separation with electron capture detection (ECD).

Four 1-L replicates of reagent water were spiked with 25 µg each of dichlone, captan, kepone, and methoxychlor and extracted serially with three 60-mL aliquots of methylene chloride. A method blank of reagent water was processed along with the samples. The extracts were combined, dried with sodium sulfate, and concentrated to approximately 5 mL using KD apparatus. The concentrated extracts were exchanged to hexane, placed on top of a column containing 20 g of Florisil, and eluted serially with 200-mL volumes of the following eluents:

Fraction 1: 6% ethyl ether in hexane
Fraction 2: 15% ethyl ether in hexane
Fraction 3: 50% ethyl ether in hexane
Fraction 4: ethyl ether
Fraction 5: 6% acetone in ethyl ether

The fractions were combined step-wise and concentrated by KD to 10.0 mL by concentrating the first 500 mL to 10-20 mL and then adding the remaining fractions. Before concentration, 2 µg of octachlorobiphenyl (IS) were added. Addition of internal standard before final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained.

Sample extracts were analyzed by GC-ECD using the following conditions:

GC:	Varian 3700
Column:	DB-5 fused silica (30 m)
Column Temperature Program:	70°C (2 min hold); 8°C/min to 275°C (5 min hold)
Detector Temperature:	320°C
Injector Temperature:	250°C
Injection Volume:	2 µL (splitless)

RESULTS AND DISCUSSION

Chromatographic Separations

The elution order and precision of retention time on the SPB-5 column for the chlorinated pesticides are shown in Table 12. A chromatogram showing the separation and peak shapes is presented in Figure 10. All four compounds were found to be well separated on the SPB-5 column with acceptable peak shapes. The peak at a retention time of 14.4 minutes in Figure 10 is believed to be a decomposition product of captan.

TABLE 12. PRECISION OF RETENTION TIME FOR CHLORINATED PESTICIDES ON SPB-5 FUSED SILICA COLUMN

Compound	Retention Time for Given Replicate, min				SD(a)	RSD%(b)
	Rep 1	Rep 2	Rep 3	Average		
Dichlone	19.22	19.23	19.23	19.23	0.006	0.03
Captan	22.75	22.75	22.75	22.75	0.000	0.00
Kepone	25.37	25.38	25.38	25.38	0.006	0.002
Methoxychlor	27.41	27.42	27.41	27.41	0.006	0.002

(a) SD = Standard Deviation.
(b) RSD% = Percent Standard Deviation.

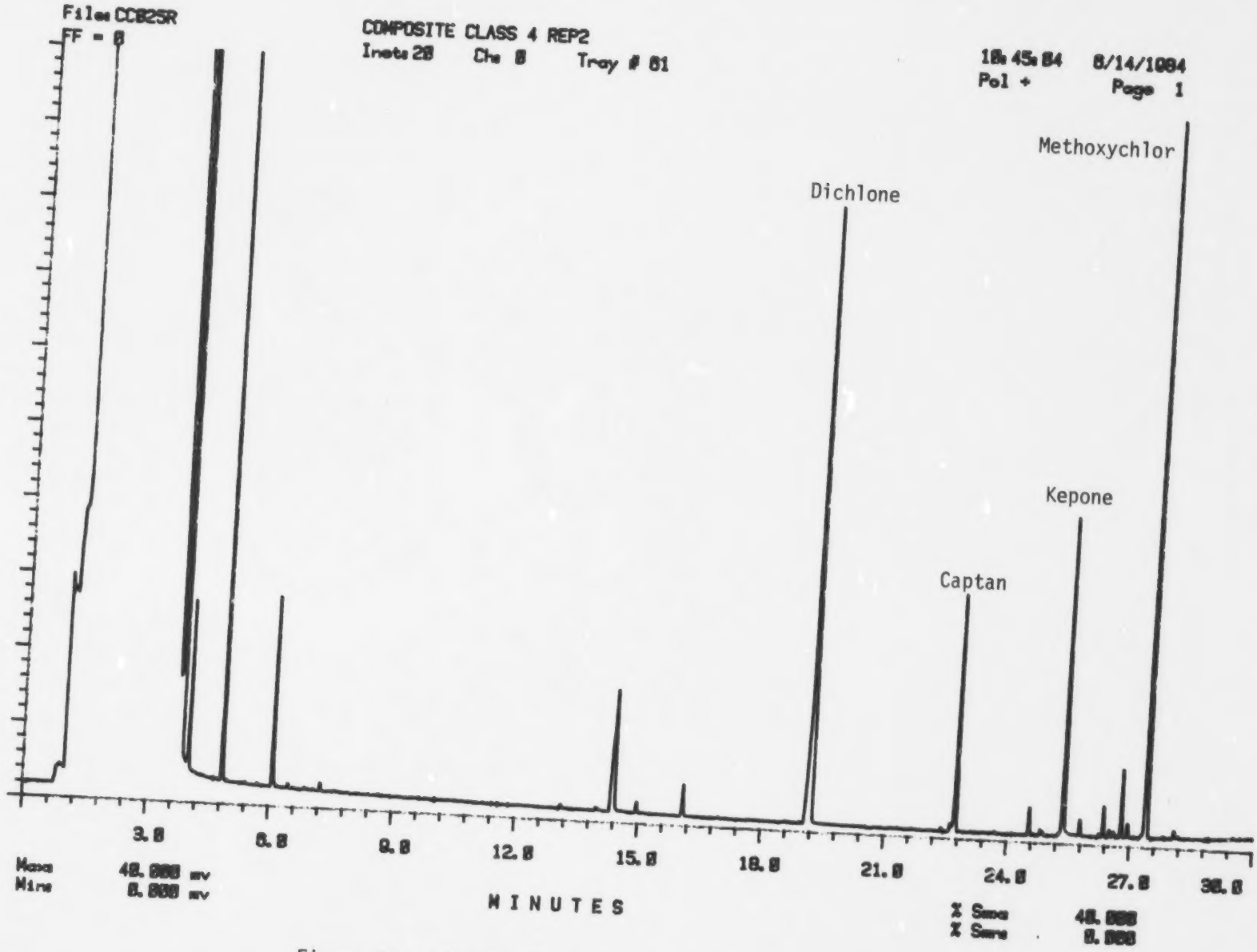

Figure 10. GC-FID chromatogram of chlorinated pesticides and related compounds.

The chromatography of these compounds was also evaluated using the Carbowax 20M fused silica capillary column. Only dichlone was found to elute from the column, with a retention time of 10.2 minutes. The other chlorinated compounds would not elute due to the higher polarity and significantly lower maximum temperature (240°C) of this column. Hence, this column was found to be unsuitable for this compound class.

Extraction Studies

The results of the extraction efficiency study for the chlorinated pesticides are presented in Table 13.

Recoveries for the chlorinated pesticides spiked at the 100 µg/L level ranged from 76.3 percent for dichlone to 92.4 percent for kepone. The precision of extraction was less than 12 percent (RSD) in all cases for these compounds. These data indicate that the neutral pH extraction procedure with methylene chloride is adequate for extraction of these compounds from aqueous solution. Other extraction techniques were not evaluated.

Evaluation of Column Cleanup Techniques

The results of the initial Florisil cleanup experiment on the four chlorinated pesticides are presented in Table 14. Methoxychlor was the only compound which was quantitatively recovered. Other compounds apparently were not eluted from the Florisil using the 50 percent ether in hexane eluent. As a result of this experiment, the elution solvents were modified to provide a more polar eluent series. The results of the second experiment using the modified elution scheme are presented in Table 15. In this experiment, 6 and 15 percent ethyl ether in hexane fractions were deleted, and elution began with the 50 percent ether in hexane fraction. As a result, the elution order was changed, in that captan and dichlone are no longer eluted in the 50 percent ethyl ether in hexane fraction. Although this could be due to slight differences in activities of the Florisil, it is probably due to the absence of the first two elution solvents from the original cleanup procedure. The data presented in Table 15 show good recovery for captan (90 percent

TABLE 13. EXTRACTION EFFICIENCY OF CHLORINATED PESTICIDES USING METHYLENE CHLORIDE AT NEUTRAL pH

Compound(a)	Spike Level, µg/L	Amount Found in Given Replicate, µg/L					Average	SD	RSD%	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5				
Dichlone	100	72.1	77.7	62.9	84.0	84.7	76.3	9.07	11.89	76.3
Captan	100	78.3	94.2	92.4	87.7	87.4	88.0	6.17	7.01	88.0
Kepone	100	86.9	85.6	103.9	85.6	100.2	92.4	8.86	9.59	92.4
Methoxychlor	100	81.5	89.5	109.1	93.4	86.6	92.0	10.49	11.40	92.0

TABLE 14. RECOVERY OF CHLORINATED PESTICIDES USING FLORISIL CLEANUP PROCEDURE

Compound	Amount Spiked, µg	Amount Found in Given Fraction, µg									Average Total Recovery, µg	SD	RSD %	Average Percent Recovery
		6% Ethyl Ether in Hexane			15% Ethyl Ether in Hexane			50% Ethyl Ether in Hexane						
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3				
Dichlone	100	--(a)	--	--	--	--	--	31	25	34	30	4.6	15	30
Captan	100	--	--	--	--	--	--	54	52	61	56	4.7	8.5	56
Kepone	100	--	--	--	--	--	--	2.8	6.5	--	4.6(b)	2.6	56	4.6
Methoxychlor	100	94	87	88	0.8	3.7	3.1	--	--	--	92	2.7	2.4	93

(a) Dash (-) indicates compound was not present in given fraction.

(b) Two replicates only.

TABLE 15. RECOVERY OF CHLORINATED PESTICIDES USING MODIFIED FLORISIL CLEANUP PROCEDURE

Compound (a)	Amount Spiked, µg	Amount Found in Given Fraction, µg									Average Total Recovery, µg	SD	RSD %	Average Percent Recovery
		50% Ethyl Ether in Hexane			100% Ethyl Ether			5% Acetone in Ethyl Ether						
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3				
Dichlone	100	--(b)	--	--	13	17	14	--	--	--	15	2.1	14	15
Captan	100	--	--	--	77	86	80	14	4.2	10	90	0.53	0.6	90
Kepone	100	--	--	--	44	52	46	5.1	3.5	5.3	52	3.3	6.3	52

(a) Methoxychlor not evaluated in this experiment.

(b) Dash (-) indicates compound was not present in given fraction.

versus only 56 percent for the original procedure). This elution scheme also provides some recovery of kepone (52 percent versus only 4.6 percent for the original procedure). However, dichlone showed lower recovery, possibly due to decomposition in the diethyl ether KD concentration step, since this fraction was concentrated (KD) separately, as were the other fractions.

Evaluation of Kuderna-Danish Concentration Recovery

All four chlorinated pesticides showed good recovery during KD concentration in 15 percent ethyl ether in hexane as shown in Table 16, but this experiment was conducted prior to the modified elution solvent experiment (described above and shown in Table 16). The recovery of these compounds in 100 percent ethyl ether with KD concentration was not evaluated by itself, but the column cleanup data described above suggest that some recovery problems may exist in this solvent when used neat.

Evaluation of Method Accuracy and Precision

The results of the precision and accuracy determinations for the chlorinated pesticides method are presented in Table 17. Recoveries for the four compounds range from 38 percent for dichlone to 92 percent for methoxychlor and are in sharp contrast to recoveries presented in Table 15 for the cleanup procedure only, which gave average total recoveries of 15, 90, and 52 percent for dichlone, captan, and kepone, respectively. The improved recoveries for the overall method appear to be due to the fact that the eluates from the Florisil cleanup were combined in the present experiment, while the ethyl ether fraction, which contains dichlone, captan and kepone, was concentrated by itself in the experiment presented in Table 15. These data suggest that these compounds are unstable in pure ethyl ether at elevated temperatures but are more stable in the mixed solvent system resulting from the combined eluents from the column cleanup procedure. The data in Table 17 suggest a problem with the values for dichlone and captan in replicate 4, and higher recoveries are obtained by deleting these two values from the statistics, as indicated by the data in parentheses in the table. The

TABLE 16. RECOVERY OF CHLORINATED PESTICIDES AFTER KUDERNA-DANISH CONCENTRATION IN 15% ETHYL ETHER IN HEXANE

Compound	Amount Spiked, µg	Amount Found in Given Replicate, µg				SD	RSD %	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Average			
Dichlone	100	91	93	93	93	1.2	1.3	93
Captan	100	111	106	110	109	2.4	2.2	109
Kepone	100	78	79	80	79	1.1	1.4	79
Methoxychlor	100	94	98	101	98	3.6	3.7	98

TABLE 17. PRECISION AND ACCURACY OF CHLORINATED PESTICIDE DETERMINATIONS

Compound	Spike Level, µg/L	Amount Found in Given Replicate, µg/L				Average	SD	RSD%	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4				
Dichlone	25	11	11	14	1.8	9.4 (12)[a]	5.2 (1.8)[a]	56 (15)[a]	38 (48)[a]
Captan	25	21	19	18	13	18 (19)[a]	3.4 (1.5)[a]	19 (7.8)[a]	71 (77)[a]
Kepone	25	18	20	18	17	18	1.2	6.7	74
Methoxychlor	25	22	25	22	22	23	1.7	7.3	92

(a) Average, SD, and RSD% without Rep 4.

replicate was not reanalyzed. Except for the low recovery for dichlone, the method as modified appears to be acceptable for the determination of these compounds. The low recovery for dichlone appears to be due to the cleanup procedure, since better recoveries were obtained using the method without cleanup. Dichlone is a quinone and, therefore, is susceptible to oxidative degradation. Furthermore, the Florisil used for cleanup could provide a catalytic surface for this degradation.

CONCLUSIONS

Determination of the four chlorinated pesticides can be accomplished by a combination of methylene chloride extraction, Florisil column cleanup, and fused silica capillary column GC with electron capture detection. Dichlone, however, gives a low recovery with this method possibly due to its succeptibility as a quinone to oxidation during the solvent evaporation step.

RECOMMENDATIONS

Decomposition of dichlone during solvent reduction deserves further investigation. Perhaps addition of an antioxidant or use of different extraction and/or cleanup solvents could eliminate this possible problem.

SECTION 7

EXTRACTABLE SEMIVOLATILE BASES

The high-interest compounds from Table 1 evaluated under this group were quinoline and strychnine. Aniline was also included in this evaluation.

EXPERIMENTAL

Chromatographic Separations

The separation of aniline, quinoline and strychnine was evaluated using reference materials in injection solvents on both the SPB-5 and Carbowax 20M fused silica capillary columns using the Table 2 instrumentation and conditions. In addition, the chromatography of these compounds on the DB-1 and Hewlett-Packard 5 percent phenyl methyl silicone fused capillary columns were also determined. An evaluation of injection conditions was not undertaken for this class of compounds. Analytes were injected singly and in mixtures in an appropriate injection solvent, generally at 50 µg/mL.

Extraction Studies

The extraction efficiency from water of the semivolatile bases was evaluated using separatory funnel extraction techniques with a variety of solvents, pH adjustments, and with the use of salting-out techniques.

Neutral pH Extraction with Methylene Chloride--

Five replicates were prepared at the 100 µg/L spike level in reagent water by the addition of 100 µL of a 1.0 mg/mL stock solution containing quinoline and strychnine (in methanol) to 1 L of reagent water. Prior to spiking, the reagent water was buffered at pH 7.0 with 1.0 mM phosphate buffer. Samples and one reagent blank were extracted

with methylene chloride, dried using sodium sulfate, and concentrated using KD techniques to approximately 10 mL. At this time, 100 µg of phenanthrene (IS) were added, and the samples concentrated to 1 mL after exchange to hexane. Addition of internal standard before final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained. Samples were analyzed by GC on the SPB-5 column using Table 2 conditions.

Acidic/Basic Extraction with Methylene Chloride--

Five replicates were prepared at the 100 µg/L spike level in 1 L of reagent water by the addition of 100 µL of a 1.0 mg/mL methanol stock solution of aniline, quinoline, and strychnine. The pH of the samples and a reagent water blank was adjusted to pH 2 using 20 percent sulfuric acid and short range pH paper, and the samples were extracted serially with three 60-mL portions of methylene chloride. The aqueous samples were then adjusted to pH 11 with 10 N sodium hydroxide using short range pH paper and again serially extracted with three 60-mL portions of methylene chloride. The basic extracts were combined, dried using sodium sulfate, and concentrated to approximately 1 mL after addition of 10 mL of 2.0 µg/mL phenanthrene (IS) using KD techniques. Addition of internal standard before final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained.

Acidic/Basic Methylene Chloride Extraction with Salting-out Step--

The above experiment was repeated using the same procedure except that no acid/neutral extraction was performed, and 200 g of reagent grade sodium chloride was added prior to pH adjustment (pH 11) and extraction of the basic aqueous sample.

Extraction with 15 Percent Methylene Chloride in Hexane Solvent--

The initial experiment was repeated using 15 percent methylene chloride in hexane as the extraction solvent, except that no acid/neutral extraction was made and no salt was added.

Extraction with Methyl t-Butyl Ether--

Four replicates containing 25 µg each of aniline, quinoline, and strychnine were prepared in 1 L of reagent water. The pH of the samples and a reagent blank was adjusted to pH 2 (pH paper) using 20 percent sulfuric acid, and the samples were extracted serially with three 60 mL portions of methyl t-butyl ether. The aqueous samples were then adjusted to pH 11 with 10 N sodium hydroxide and again serially extracted with three 60-mL portions of methyl t-butyl ether. The basic extracts were combined, dried over sodium sulfate, concentrated by KD techniques, exchanged to hexane, and analyzed by GC (described previously). Phenanthrene (20 µg/sample) was added prior to KD concentration to serve as internal standard (IS). Addition of internal standard before final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained.

Evaluation of Concentration Techniques

Rotary Evaporation Concentration--

To evaluate the possibility that strychnine was lost due to decomposition at the elevated temperatures used in the KD concentration step, an experiment was performed in which 100 ug of aniline, quinoline, and strychnine standard and 20 µg of phenanthrene (IS) were concentrated just to dryness at 40°C using rotary evaporation from a volume of 180 mL of methylene chloride. After evaporation, 1.5 mL of hexane were added and the sample transferred to a GC vial for GC analysis as described previously.

Kuderna-Danish Concentration Recovery--

To evaluate strychnine recovery on KD concentration, two replicate samples were prepared by placing 100 µg each of aniline, quinoline, and strychnine in 180 mL of methylene chloride. After adding 20 µg of phenanthrene (IS) to each sample, they were concentrated to 1.0 mL by KD techniques and analyzed by GC. To evaluate the KD concentration recovery of strychnine in diethyl ether, a potential extraction solvent,

two samples containing 100 ug of strychnine and 20 µg of phenanthrene (IS) in 180 mL of diethyl ether were prepared. The samples were concentrated to 1 mL in KD apparatus and analyzed as described above. In these experiments, addition of internal standard before final concentration is a deviation from standard EPA methodology, but it is not expected to have any effect on the results obtained. This experiment was repeated with three replicate samples containing 100 µg of aniline, quinoline, and strychnine in methyl t-butyl ether.

RESULTS AND DISCUSSION

Literature Review

In the report provided by EMSL-Cincinnati (2), quinoline was found to extract with acceptable recoveries (greater than 70 percent) from both distilled water and secondary effluent, and no problems were anticipated in including this compound in the class with the other two extractable semivolatile bases, aniline and strychnine.

Chromatographic Separations

The elution order and precision of retention time for the extractable semivolatile bases obtained using the SPB-5 column are presented in Table 18.

TABLE 18. PRECISION OF RETENTION TIME FOR EXTRACTABLE SEMIVOLATILE BASES ON SPB-5 FUSED SILICA COLUMN

Compound	Retention Time for Given Replicate, min			Average	SD(a)	RSD%(b)
	Rep 1	Rep 2	Rep 3			
Aniline	6.56	6.53	6.55	6.55	0.0153	0.23%
Quinoline	11.55	11.53	11.54	11.54	0.010	0.09%
Strychnine	37.98	37.96	37.96	37.97	0.0115	0.03%

(a) SD = standard deviation.
(b) RSD = percent relative standard deviation.

These compounds chromatograph over a very wide range on the SPB-5 column, with aniline eluting at 6.55 minutes and strychnine at 37.97 minutes. Individual compounds from this group were found to be chromatographically pure, with minor peaks in the chromatogram being less than 5 percent of the major peak in all cases. The precision of retention time was good and less than 0.25 percent relative standard deviation (RSD) in all cases. A chromatogram of a mixture of the three compounds of this class on a 5 percent phenyl methyl silicone column which is essentially identical to the SPB-5 column is presented in Figure 11. The chromatography of this class of compounds was evaluated on the Carbowax 20M fused silica capillary column and was found to be unsuitable due to the inability to elute strychnine. Strychnine was found to elute from the SPB-5 column after about five minutes at 300°C and will not elute from the polar Carbowax column, since the maximum temperature which can be used is 240°C. Aniline eluted with a retention time of 14.0 minutes, and quinoline with a retention time of 16.5 minutes on the Carbowax column using the standard conditions given previously.

The separation of the three bases on the DB-1 fused silica capillary column was similar to that obtained on the SPB-5 column with essentially identical relative retention values. For the DB-1 column, a maximum temperature of 310°C was used instead of the 300°C maximum

temperature for the SPB-5 column. Otherwise, the conditions were the same.

Extraction Studies

Neutral pH Extraction with Methylene Chloride--

The results of the extraction efficiency study for the two semivolatile compounds evaluated are presented in Table 19. Recoveries for the two semivolatile bases evaluated at pH 7 were 108 percent for quinoline and 46 percent for strychnine.

Acidic/Basic Extraction with Methylene Chloride--

The results for the basic fractions from the acidic/basic extraction with methylene chloride are presented in Table 20.

These data show acceptable recovery for aniline and quinoline, but only about 52 percent recovery for strychnine. Since the acid/neutral fractions were not saved in this experiment, the experiment was repeated to evaluate losses to that fraction, and the results of this new experiment are presented in Tables 21 and 22.

The data in Table 21 show that the strychnine was not lost to the acid/neutral fraction during extraction, and the data from Table 22 are similar to those presented in Table 20.

Acid/Base Methylene Chloride Extraction with Salting-out Step--

The data for the extractability experiment where 20 percent sodium chloride was added prior to methylene chloride extraction of the basic aqueous phase are presented in Table 23. Recovery for strychnine was no better using this approach.

Extraction Using 15 Percent Methylene Chloride in Hexane as Solvent--

Data from the extraction experiment with 15 percent methylene chloride in hexane are presented in Table 24.

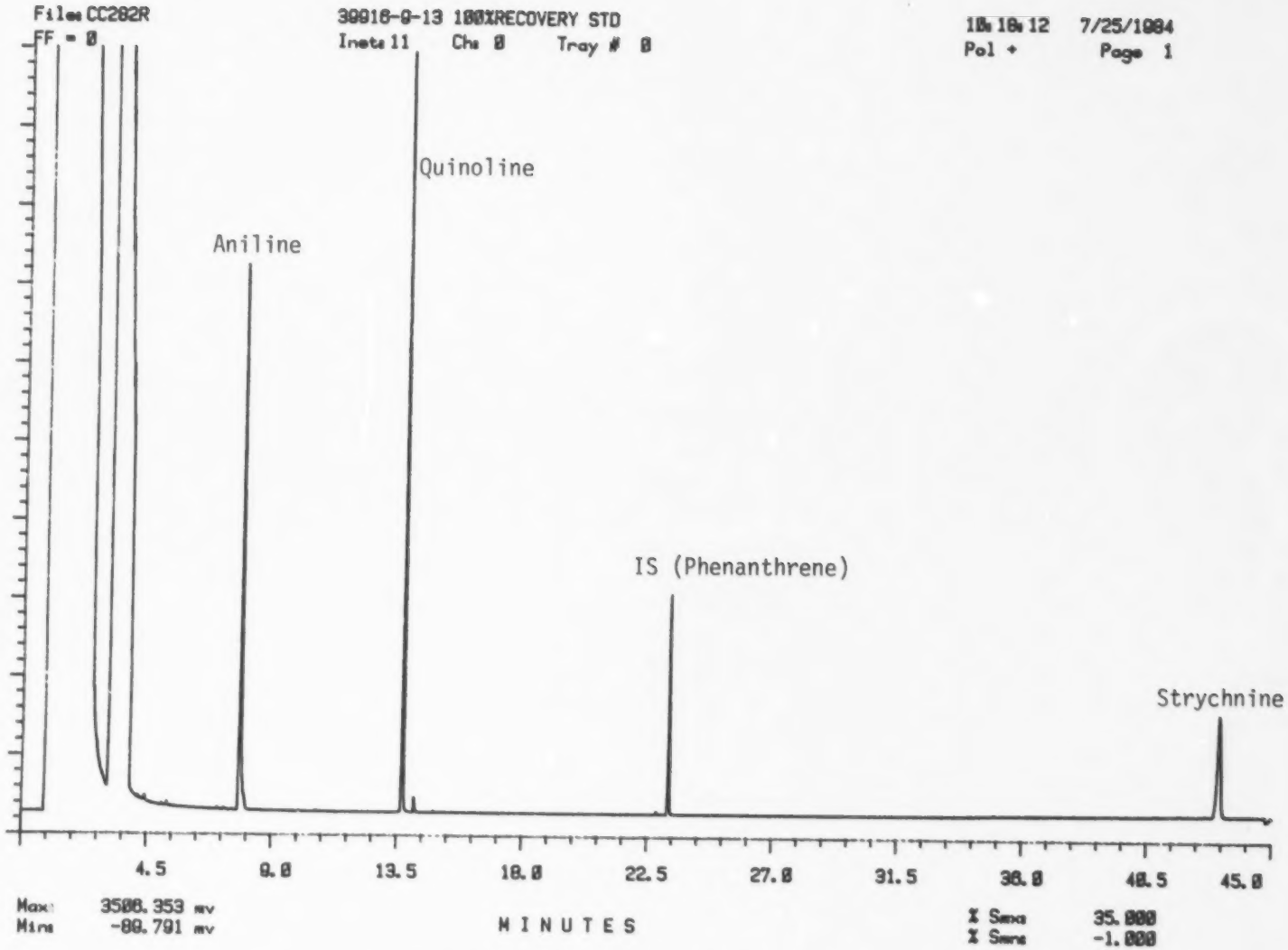

Figure 11. GC-FID chromatogram of the extractable semivolatile bases.

TABLE 19. EXTRACTION EFFICIENCY OF SEMIVOLATILE BASES USING METHYLENE CHLORIDE AT NEUTRAL PH

Compound(a)	Spike Level, µg/L	Amount Recovery in Given Replicate, µg/L					Average	SD	RSD, Percent	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5				
Quinoline	100	96.6	114	111	109	110	108	6.2	5.8	108
Strychnine	100	27.8 (b)	44.6	49.7	46.1	44.3	46.2	2.5	5.4	46.2

(a) Aniline was not included in this study.
(b) Rejected as an outlier since this value differs from the mean of Reps 2-5 by 7.4 times the standard deviation of Reps 2-5.

TABLE 20. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES FROM REAGENT WATER USING ACIDIC/BASIC EXTRACTION WITH METHYLENE CHLORIDE

Compound	Spike Level, µg/L	Amount Found in Basic Extract for Given Replicate, µg/mL					Average	SD	RSD%	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5				
Aniline	100	83.9	85.0	88.3	94.2	94.0	89.1	4.86	5.0	89.1
Quinoline	100	75.8	81.4	83.7	87.4	88.3	83.3	5.05	6.0	83.3
Strychnine	100	56.0	44.2	50.0	48.4	60.4	51.8	6.41	12.0	51.8

(a) Acid/neutral fraction extracted first rather than base/neutral fraction.

TABLE 21. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES IN ACID/NEUTRAL EXTRACT FROM REAGENT WATER USING ACIDIC/BASIC EXTRACTION WITH METHYLENE CHLORIDE

Compound	Spike Level, µg/L	Amount Found in Acid/Neutral Extract for Given Replicate, µg/mL				Average	SD	RSD%	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4				
Aniline	100	1.1	1.1	1.0	--[a]	1.1	0.04	3.8	1.1
Quinoline	100	1.5	1.4	1.5	--	1.5	0.05	1.0	1.5
Strychnine	100	0.75	0.59	0.58	--	0.64	0.095	15.0	0.64

(a) This extract replicate lost during preparation.

TABLE 22. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES IN BASIC EXTRACT FROM REAGENT USING ACIDIC/BASIC EXTRACTION WITH METHYLENE CHLORIDE

Compound	Spike Level, µg/L	Amount Found in Basic Extract for Given Replicate, µg/mL				Average	SD	RSD%	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4				
Aniline	100	88.9	91.4	92.0	91.7	91.0	1.42	1.56	91.0
Quinoline	100	93.8	93.4	93.6	94.6	93.8	0.52	0.56	93.8
Strychnine	100	58.0	49.7	62.6	61.1	57.9	5.77	9.97	57.9

TABLE 23. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES FROM REAGENT WATER USING ACIDIC/BASIC METHYLENE CHLORIDE EXTRACTION WITH SALTING-OUT STEP ADDED

Compound(a)	Amount Found in Basic Extract for Given Replicate, µg/mL				Average	SD	RSD%	Average Percent Recovery
	Rep 1	Rep 2	Rep 3	Rep 4				
Aniline	107.8	102.7	97.4	109.0	103.5	6.62	6.39	103.5
Quinoline	100.7	96.8	92.4	101.4	97.8	4.12	4.21	97.8
Strychnine	34.6	62.9	36.9	52.6	46.7	13.4	28.75	46.7

(a) All compounds spiked at 100 µg/L.

TABLE 24. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES FROM REAGENT WATER USING EXTRACTION WITH 15 PERCENT METHYLENE CHLORIDE IN HEXANE

Compound(a)	Amount Found in Basic Extract for Given Replicate, µg/mL				Average	SD	RSD%	Average Percent Recovery
	Rep 1	Rep 2	Rep 3	Rep 4				
Aniline	27.6	22.4	22.7	23.4	24.0	2.41	10.1	24.0
Quinoline	99.5	95.1	92.2	96.9	95.9	3.10	3.23	95.9
Strychnine	35.9	34.0	42.2	38.0	37.5	3.54	9.44	37.5

(a) All compounds spiked at 100 µg/L.

These data demonstrate that methylene chloride is a much better extraction solvent for aniline and strychnine than 15 percent methylene chloride in hexane. Extractability of quinoline is equivalent using either of the two solvent systems.

Extraction of Semivolatile Bases using Methyl t-Butyl Ether--

The results of the extraction/cleanup experiment for aniline, quinoline, and strychnine using methyl t-butyl ether rather than methylene chloride are presented in Table 25. Quantitative recovery was again found for both aniline and quinoline, but strychnine was found to extract at a much lower level than was observed for methylene chloride (9.6 percent versus approximately 40 to 50 percent in the previous studies). These data indicate that this solvent is unsuitable for the extraction of strychnine, although acceptable recoveries were found for aniline and quinoline.

Evaluation of Concentration Techniques

Rotary Evaporator Concentration--

The results of the rotary evaporation concentration experiment for aniline, quinoline, and strychnine are presented in Table 26. Erratic recoveries were obtained for all three analytes and indicate that rotary evaporation is not appropriate for extract concentration, since much more reproducible results were obtained using KD concentration. The poor recoveries are probably due to losses on drying in the evaporator flask.

Kuderna-Danish Concentration Recovery--

The results of the experiment to evaluate the recovery of strychnine during KD concentration are presented in Table 27. These data indicate that either strychnine is decomposed during concentration or it is tied up as the salt from traces of hydrochloric acid in the methylene chloride and is not chromatographed. However, since the methylene chloride is equilibrated with water during the extraction of the compounds under basic conditions, it is unlikely that any significant amounts of hydrochloric acid or any other acid are carried

TABLE 25. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES WITH EXTRACTION USING METHYL t-BUTYL ETHER

Compound	Spike Level, µg/L	Amount Found in Given Replicate, µg/L							Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4	Average	SD	RSD %	
Aniline	25	24	19	19	18	20	2.7	13	80
Quinoline	25	25	23	23	24	24	1.2	4.9	96
Strychnine	25	1.8	0.6	1.6	5.6	2.4	2.2	93	9.6

TABLE 26. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES AFTER ROTARY EVAPORATION CONCENTRATION IN METHYLENE CHLORIDE

Compound	Spike Level, µg/L	Amount Found in Given Replicate, µg/L				Average	SD	RSD%	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Rep 4				
Aniline	100	30.1	20.3	15.7	44.7	40	23	58	40
Quinoline	100	54.3	87.5	36.0	66.7	61	21	35	61
Strychnine	100	72.4	46.0	39.9	33.9	48	17	35	48

over to the organic phase during extraction. It therefore follows that the losses are due to either strychnine decomposition or methylene chloride decomposition.

The results of the KD concentration experiment for strychnine in ethyl ether resulted in complete loss of strychnine in two replicates, presumably due to decomposition as a result of peroxide formation of the ether.

The results of the KD concentration experiment using methyl t-butyl ether for aniline, quinoline, and strychnine are presented in Table 28. These data indicate that all three compounds are stable in this solvent. This is the first solvent evaluated which allows for quantitative recovery of strychnine during the concentration step. Unfortunately this solvent could not extract strychnine from water.

Further experiments with this class of compounds were not conducted due to the inability to obtain quantitative extraction of strychnine.

TABLE 27. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES AFTER KUDERNA-DANISH CONCENTRATION IN METHYLENE CHLORIDE

Compound	Amount Spiked, µg	Amount Found in Given Replicate, µg			Average Percent Recovery
		Rep 1	Rep 2	Average	
Aniline	100	124.3	123.1	123.7	123.7
Quinoline	100	108.8	107.0	107.9	107.9
Strychnine	100	47.2	43.3	45.3	45.3

CONCLUSIONS

Aniline and quinoline are recovered well using standard extraction techniques, but strychnine could not be recovered at greater than about 50 percent using a variety of extraction solvents.

RECOMMENDATIONS

Work needs to be done to improve extraction conditions for strychnine. One approach might be the use of aromatic solvents such as benzene, toluene and pyridine (as a modifier). However, these solvents would probably present problems to the solvent reduction step due to their low volatility.

TABLE 28. RECOVERY OF EXTRACTABLE SEMIVOLATILE BASES AFTER KUDERNA-DANISH CONCENTRATION IN METHYL t-BUTYL ETHER

Compound	Spike Level, µg	Amount Found in Given Replicate, µg				SD	RSD %	Average Percent Recovery
		Rep 1	Rep 2	Rep 3	Average			
Aniline	100	92	83	87	87	4.3	4.9	87
Quinoline	100	105	102	101	102	2.0	2.0	102
Strychnine	100	89	89	100	93	6.1	6.7	93

SECTION 8

VOLATILE COMPOUNDS

The compounds considered amenable to purge-and-trap gas chromatographic analysis were subdivided into two groups: (1) nonpolar volatile compounds (Table 29) which could be analyzed using room-temperature sparging; and (2) polar volatile compounds (Table 30) to be analyzed using elevated-temperature sparging.

TABLE 29. NONPOLAR VOLATILE COMPOUNDS

Methyl mercaptan*	Isoprene
Propylene oxide*	Cyclohexane
Allyl chloride	o-Xylene
Ethyl ether	

* High-interest compound

TABLE 30. POLAR VOLATILE COMPOUNDS

Acetone	Epichlorohydrin
Methyl ethyl ketone	Allyl alcohol*
Methyl isobutyl ketone	Vinyl acetate
Methyl butyl ketone	Butyl acetate
Dioxane	Amyl acetate

* High-interest compound

EXPERIMENTAL

Chromatographic Separations

The volatile compounds, except for methyl mercaptan, were prepared as individual standards in CS_2 at 1.0 mg/mL. Literature densities were used to compute the volumes of neat reagent required to prepare these solutions. Separate aqueous mixtures of the polar compounds were similarly prepared at the same concentration level. Compounds were analyzed individually and as mixtures by direct injection using a Hewlett-Packard 5730 GC with FID detection and the following two chromatographic columns:

Column 1 - 6 ft x 2 mm ID, glass; 1% SP1000 on Carbopak B, 60/80 mesh

Column 2 - 6 ft x 2 mm ID, glass; 10% Carbowax 20M on Supelcoport, 80/100 mesh.

The GC conditions employed for both columns were the following:

Sample Volume:	- 0.5 µL via auto injector
Carrier Gas:	- Helium at 30 mL/min
Zone Temperatures:	- 200°C injector; 250°C detector
Oven Program:	- 40°C for 2 min; 40 to 220°C at 8°C/min; 220°C for 16 min

In addition, preliminary experiments were performed to evaluate the efficacy for the volatile compounds using a Porapak QS column, 10 ft x 2 mm ID, and a Varian 1400 GC with FID. Two mixtures of four compounds each at 100 ug/mL in CS_2 were prepared. One mixture contained methyl mercaptan, cyclohexane, butyl acetate, and amyl acetate; the other contained propylene oxide, vinyl acetate, allyl alcohol, and o-xylene. These mixtures were analyzed in replicate with 3-µL injections using the oven program: 70 to 230°C at 10°C/min and hold at 230°C for 15 min.

Examination of Trap Breakthorugh

A "T" fitting equipped with an injection septum was installed in the line between the purge vessel outlet and the six-port valve of the Tekmar LSC-2 purge-and-trap unit. The adsorption/desorption trap was installed in the LSC-2 with the trap outlet coupled directly to the FID detector via 1/8" tubing. The trap was packed with 1 cm 3% OV-1, 7.7 cm Tenax, 7.7 cm silica gel, and 7.7 cm activated carbon (3-component trap) to test the nonpolar compounds, and with 1 cm 3% OV-1 and 23 cm Tenax (all-Tenax trap) to test the polar compounds. The purge flow rate was set at 40 mL/min, and 5 mL of reagent water was present in a standard purge vessel to provide water saturated purge gas. The purge vessel was operated at room temperature for the nonpolar compounds and at 85°C for the polar compounds. Trap breakthrough was checked by injecting 1 µL of neat analyte or high level aqueous solutions into the flowing purge gas via the injection "T". If trap breakthrough was not observed at the FID within 20 min, the instrument was put into the trap bake mode at 210°C until elution was observed.

Only the most volatile compounds were checked for trap breakthrough: methyl mercaptan, propylene oxide, allyl chloride, and isoprene for the nonpolar compounds and acetone, allyl alcohol and methyl ethyl ketone for the polar compounds. Propylene oxide was also checked with the 85°C purge setup. The nonpolar compounds were tested by injecting 1.0 µL of neat analyte into the pre-trap stream (except for methyl mercaptan, which was a 10 percent aqueous solution). The polar compounds were all tested with 1 percent aqueous solutions and acetone was also tested with a 0.1 percent aqueous solution; both solutions were injected at the 1.0 uL level (10 µg and 1.0 µg, respectively).

Purging and Desorption Efficiency

In addition to the trapping efficiency, purging and desorption efficiencies must be considered in evaluating the overall efficiency of delivery to the GC column of analytes contained in a water sample. The purging efficiency is checked by comparing the responses of detected

analytes from the usual analysis of a purge/trap/desorb standard with those from an analysis in which the analytes are injected into a septum-equipped T-fitting in the transfer line between the purge vessel and the trap. To check the desorption efficiency, a septum injection of the analytes is compared to analyses in which the same standard is injected into the T-fitting.

Purging efficiencies for the nonpolar compounds were determined in two sets. The first set included all compounds except methyl mercaptan. The second set consisted of methyl mercaptan only. A methanol stock solution was prepared by adding (volumetrically) 100 mg of each analyte (propylene oxide, allyl chloride, ethyl ether, isoprene, cyclohexane, and o-xylene) to 10.0 mL methanol for a concentration of 10 mg/mL of each. Each day that samples were analyzed, a fresh aqueous working standard (50 µg/mL) was prepared from the methanol stock in a headspace-free manner using a 5-mL gas-tight syringe containing a Teflon O-ring as a stirring device. A methyl mercaptan stock solution was prepared from neat analyte by bubbling the gas into tetraglyme to achieve a 50 mg/mL concentration. Aqueous working standards were prepared in a gas-tight 5-mL syringe (as above) by adding 25 µL of the tetraglyme stock to give a working standard at 250 µg/mL concentration.

Purged samples consisted of 5 mL of reagent water to which 10 µL of aqueous working standard were added to give either a 100 µg/L sample (all compounds except methyl mercaptan) or a 500 µg/L sample (methyl mercaptan). These aqueous working standards were also used as a calibration standard by direct septum injection of 5.0 µL in triplicate. In addition, triplicate samples of the 10 µL working standards were injected into the purge flow line after the purge vessel to provide a sample for adsorption/desorption that represented 100 percent purging efficiency.

The analysis conditions were:

Purge:	- 30 mL/min, helium, for 10 min at room temperature
Trap:	- 3-component operated at room temperature (26 to 30°C)
Desorption:	- 2.0 min at 180°C
GC column:	- 6 ft by 2 mm ID glass; 1 percent SP1000 on Carbopak B, 60/80 mesh
GC conditions:	- Helium at 30 mL/min. program: 2.0 min at room temperature (during desorption); 40°C to 220°C at 8°C/min; hold at 220°C for 10 min.

For the polar compounds, an aqueous stock solution at 1.0 mg/mL was prepared from the neat analytes in a 5-mL gas-tight syringe equipped with a valve to eliminate exposure of the stock solution to headspace. Each analyte was added by injecting 5 mg of the neat analyte (based on literature densities) into the 5-mL syringe. Mixing was accomplished with a Teflon O-ring contained in the syringe. A 50-µg/mL aqueous working standard was freshly prepared from the 1.0 mg/mL aqueous stock each day that samples were analyzed. Purged samples consisted of 10 µL of the 50 µg/mL working standard in 5.0 mL (100 µg/L) of reagent water. Purged samples were analyzed in triplicate using the conditions given in the preceding paragraph except that the all-Tenax trap was used and data sets were produced for both room temperature and 85°C purging.

The 50 µg/mL aqueous working standard was used as a calibration standard by direct septum injection of 5.0 µL in triplicate. In addition, triplicate samples of the 10-µL working standard were injected into the purge flow line after the purge vessel to provide a sample for adsorption/desorption that represented 100 percent purging efficiency.

Estimation of Detection Limit

A methanol stock solution mixture containing the nonpolar compounds (except methyl mercaptan) was prepared and diluted (in methanol) to provide a spiking standard containing propylene oxide at 4.0 µg/mL and the other analytes at 1.0 µg/mL. This working standard was used (5.0 µL) to spike 5-mL samples of reagent water to provide five replicates of detection limit assessment samples at the 1.0 µg/L level (4.0 µg/L for propylene oxide). The same working standard was also used to spike purged calibration standards at the 0.6, 2.0 and 6.0 µg/L levels (2.4, 8.0 and 24 µg/L for propylene oxide). The two lower level calibration standards were analyzed in duplicate.

For the polar compounds, a 50 µg/mL aqueous working standard was freshly prepared as described above for the purging efficiency assessment of these compounds. Duplicate purge-and-trap analyses were performed using this standard at the 5 µg/L and 30 µg/L levels to assess approximate detection limits. Based on the results at these two levels, a new stock solution in methanol containing the polar compounds (plus propylene oxide) at the following levels was prepared: 2.0 mg/mL for methyl ethyl ketone, methyl isobutyl ketone, 2-hexanone and butylacetate; 4.0 mg/mL for amyl acetate; 10.0 mg/mL for propylene oxide, acetone and vinyl acetate; 20 mg/mL for epichlorohydrin and dioxane; and 100 mg/mL for allyl alcohol. A dilution of 5 µL of this methanol stock solution into 10.0 mL of water produced the working standard of which 3, 10 and 30 µL were used in 5.0-mL purged calibration standards and 5.0 µL was used to spike 5.0-mL aliquots of reagent water for triplicate analysis to assess the detection limit. These replicate detection limit samples thus contained the analytes at µg/L levels which are numerically the same as the working standard levels noted above (4.0 to 100 µg/L).

RESULTS AND DISCUSSION

Chromatographic Separations

Based on the results of the preliminary examination of the Porapak QS column, it was clear that this GC packing would not be suitable for the wide volatility range of the analytes of interest. This finding is not surprising, since macroreticular packings generally provide the best results when used isothermally or over very narrow temperature programming limits. In programming from 70 to 230°C, the baseline drift was approximately 8-fold greater than that observed for the SP1000 column, and, even then, amyl acetate and o-xylene required about 20 minutes to elute at the upper temperature (230°C). Because these performance characteristics were not acceptable for the final method for volatile compounds, work to characterize this chromatography system was terminated.

GC retention results for the two primary columns of interest are summarized in Table 31 for the nonpolar volatile compounds and in Table 32 for the polar volatile compounds. These results indicate that the column containing 1 percent SP1000 on Carbopack B is acceptable for both compound sets. Example chromatograms for this column are shown in Figure 12 and Figure 13 for the nonpolar and polar compounds, respectively. Chromatograms for the second column packing (10 percent Carbowax 20M) are shown in Figure 14 for the nonpolar compounds and in Figure 15 for the polar compounds. While a backup GC column for these compounds would be highly desirable, the 10 percent Carbowax 20M column is clearly unacceptable, and we are not aware of any other column packing types that are expected to perform acceptably over the wide volatility range as well as to perform reliably after repeated exposure to the large amounts of water transferred to the column during trap desorption. Using the same conditions as those for Figures 12 and 13, purities of the reference materials were checked by analyzing each compound separately on both of the GC columns. None of these purity check chromatograms indicated the presence of impurities above the 1 percent level.

TABLE 31. RETENTION TIMES FOR NONPOLAR VOLATILE COMPOUNDS

Compound	Retention Time, min	
	Column 1[a,b]	Column 2[b,c]
Methyl mercaptan	1.85	0.5
Propylene oxide	5.11	0.67[d]
Allyl chloride	8.85	0.88
Ethyl ether	11.09	0.45[e]
Isoprene	13.17	0.45[e]
Cyclohexane	13.62	0.67[d]
o-Xylene	31.40	7.55

(a) 6 ft x 2 mm ID, 1% SP1000 on Carbopack B, 60/80 mesh. Except for methyl mercaptan, all compounds were analyzed in a single mixture. All retention values are the average value from two or three replicates.

(b) GC program: 40°C, 2 min; 40 to 220°C at 8°C/min; hold at 220°C for 16 min. Carrier: Helium at 30 mL/min

(c) 6 ft x 2 mm ID, 10% Carbowax 20M on Supelcoport, 80/100 mesh. Retention values are for separate analyses of each compound.

(d,e) These compounds were found to co-elute when analyzed in a mixture of all compounds.

TABLE 32. RETENTION TIMES FOR POLAR VOLATILE COMPOUNDS

Compound	Retention Time, min	
	Column 1[a,b]	Column 2[b,c]
Acetone	6.69	1.15
Allyl alcohol	9.47	5.80
Methyl ethyl ketone	11.80	1.77[d]
Epichlorohydrin	12.61	8.04
Dioxane	13.23	4.13
Vinyl acetate	13.65	1.69[d]
Methyl isobutyl ketone	19.89	3.29
Methyl butyl ketone	21.43	4.88[e]
Butyl acetate	22.56	4.93[e]
Amyl acetate	27.43	7.61

(a) 6 ft x 2 mm ID, 1% SP1000 on Carbopack B, 60/80 mesh. Retention values are from a single analysis of a mixture.

(b) GC program: 40°C, 2 min; 40 to 220°C at 8°C/min; hold at 220°C for 16 min.

(c) 6 ft x 2 mm ID, 10% Carbowax 20M on Supelcoport, 80/100 mesh. Retention values are for separate analyses of each compound.

(d,e) These compounds were not separated from each other on this column when injected together.

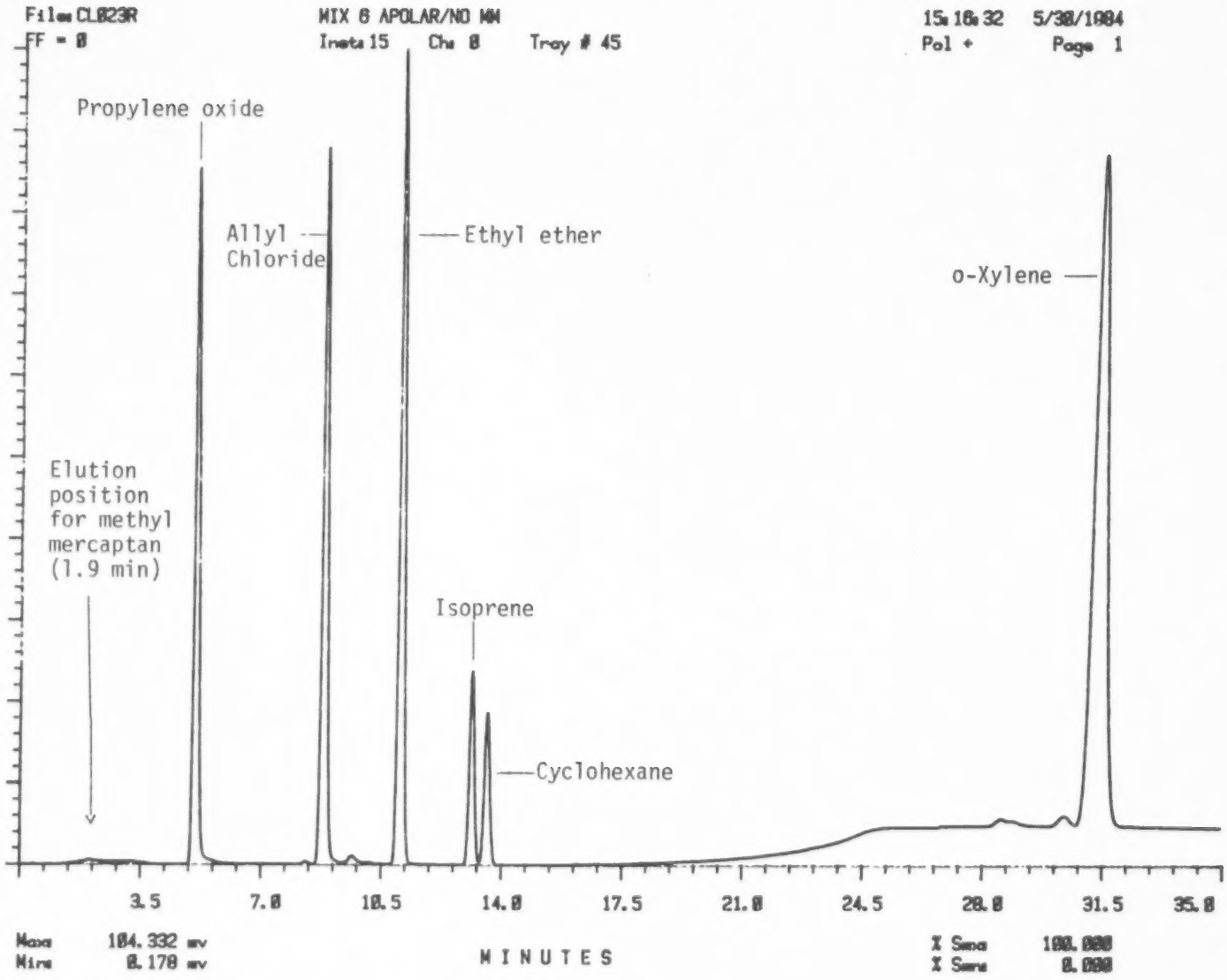

Figure 12. GC-FID chromatogram of nonpolar volatile compounds on the method 601 column; methyl mercaptan omitted.

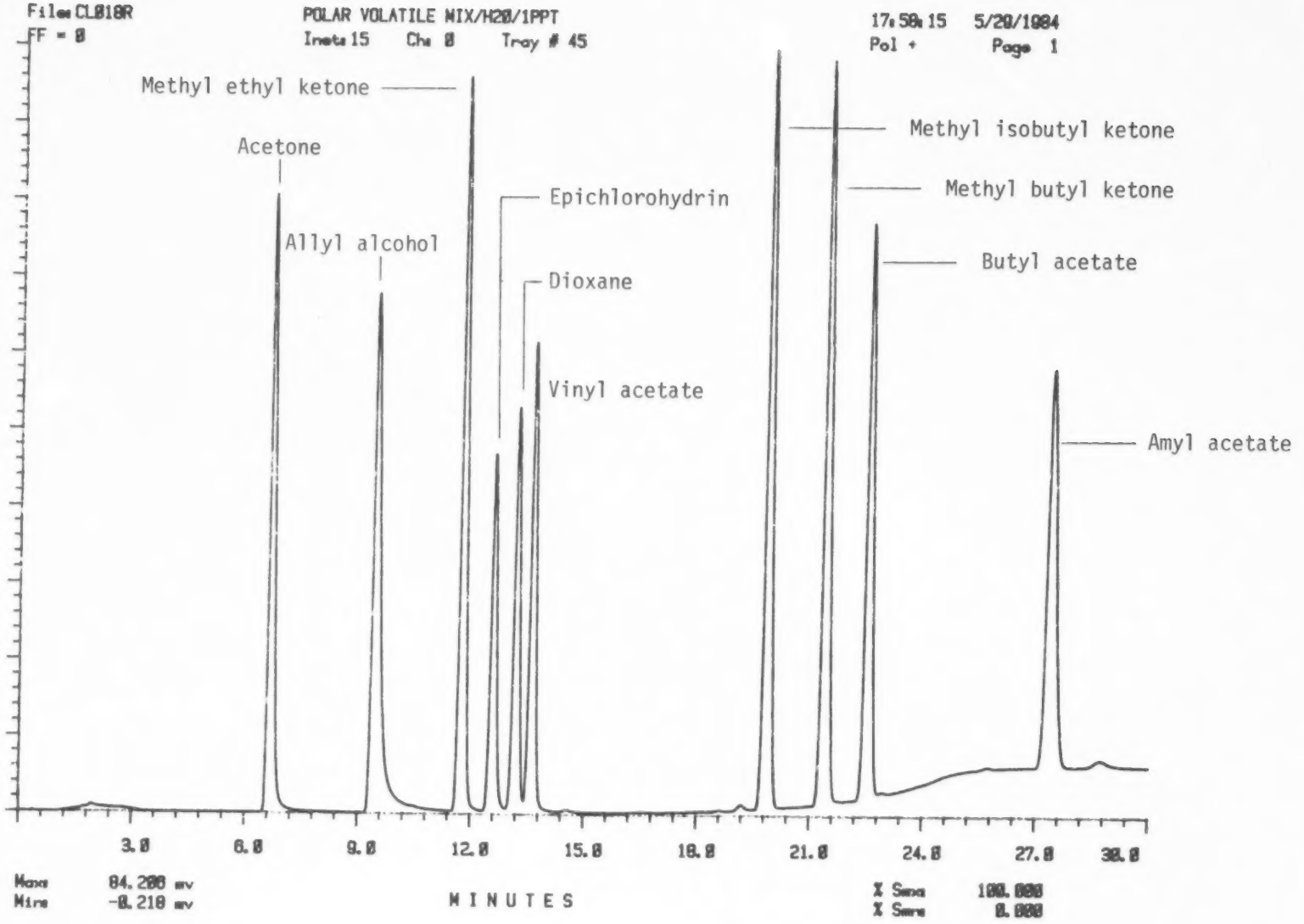

Figure 13. GC-FID chromatogram of polar volatile compounds on the method 601 column.

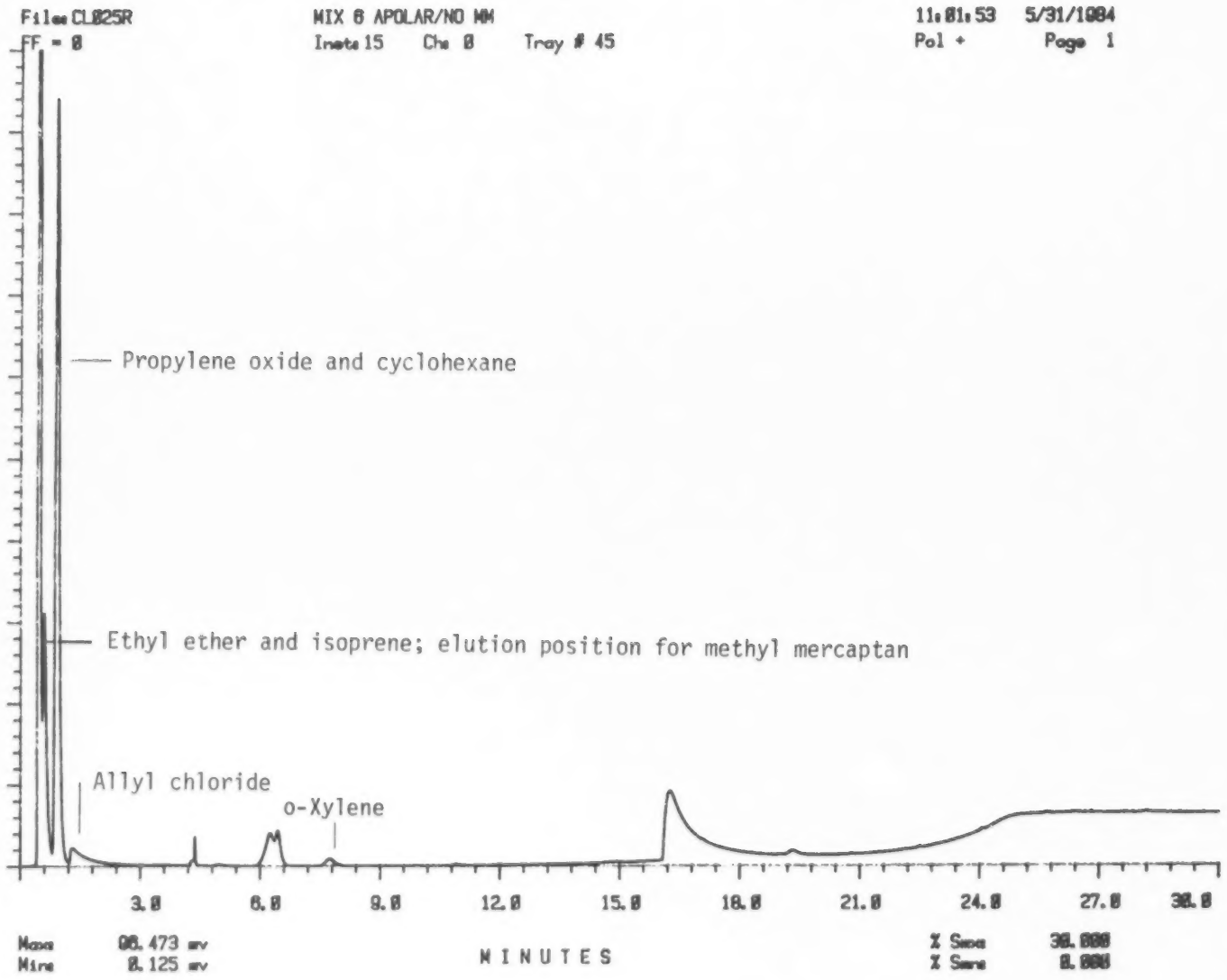

Figure 14. GC-FID chromatogram of nonpolar volatile compounds on 10% carbowax 20M; methyl mercaptan omitted.

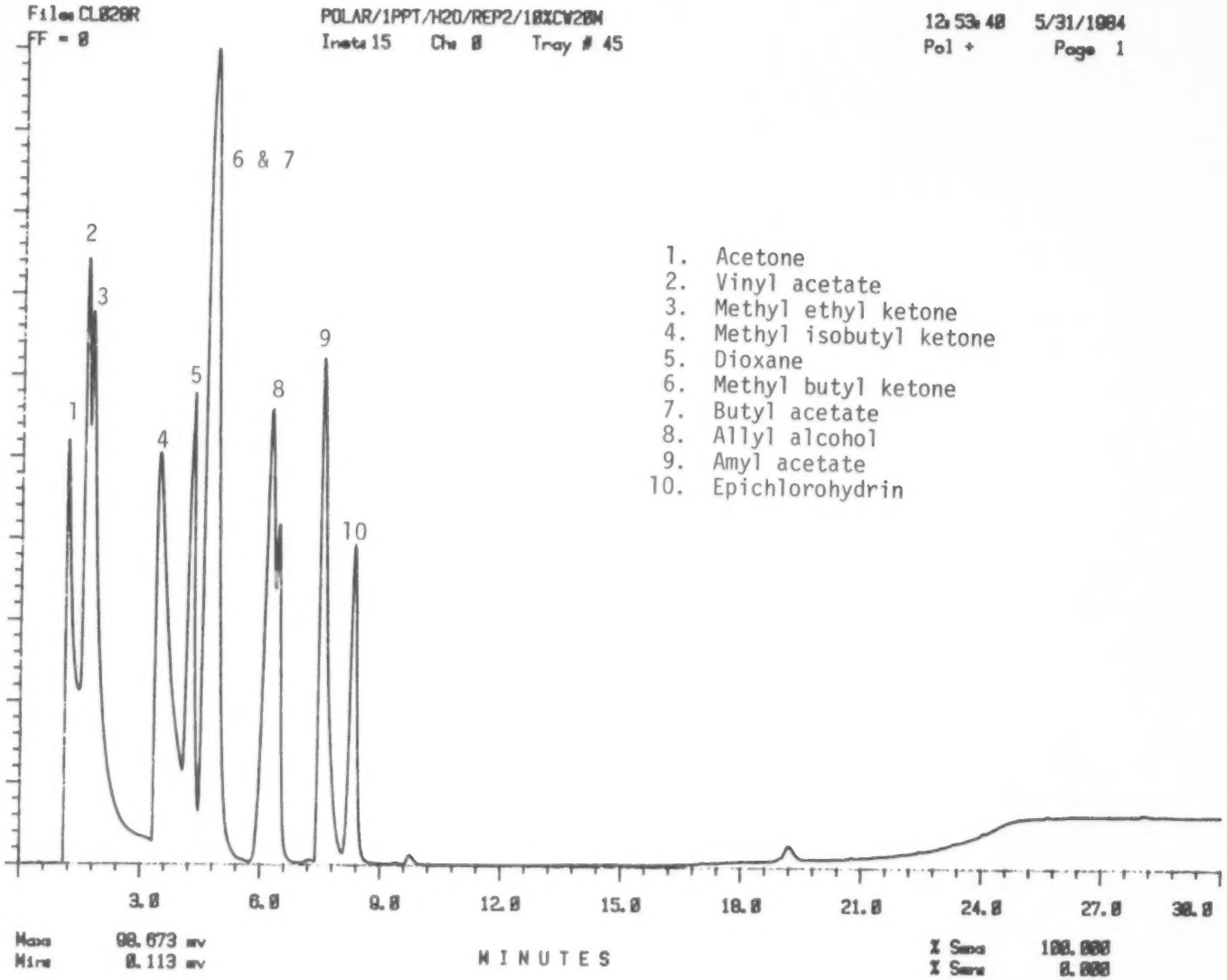

Figure 15. GC-FID chromatogram of polar volatile compounds on 10% carbowax 20M.

Examination of Trap Breakthrough

For the nonpolar compounds, none of the four compounds checked (methyl mercaptan, propylene oxide, allyl chloride, and isoprene) had breakthrough volumes less than 1600 mL with a room temperature trap (less than 30°C). Anticipated purge conditions (30 mL/min for 10 to 15 minutes) will result in a total purge volume of only 300 to 450 mL. Thus, trap breakthrough is clearly of no concern for these compounds. This result is fully expected since the trap used contains both silica gel and activated carbon. For polar compounds, the trap used is essentially all Tenax, and trap breakthrough is expected to be more probable. Allyl alcohol and methyl ethyl ketone did not exhibit any trap breakthrough up to a purge volume of 800 mL. Therefore, the other more polar and/or less volatile compounds were not checked for trap breakthrough. In a duplicate experiment, acetone, at the 10 µg level, exhibited breakthrough at 400 mL using a room temperature purge vessel to saturate the purge gas with water vapor. Under the same conditions, duplicate injections of 1.0 µg of acetone broke through the trap at 560 mL. This indicated that the breakthrough of the 10 µg sample was indeed due to adsorption capacity overload rather than a low k' value. The 1.0 µg experiment was repeated using a purge vessel at 85 $\pm$ 2°C to ensure that a higher level of water vapor in the flow exiting the purge vessel would not cause a significant difference in the breakthrough characteristics; once again, the breakthrough volume was found to be 560 mL. The temperature of the trap, as indicated by the Tekmar LSC-2 readout, ranged from 24° to 30°C, and no variation in breakthrough volume was observed over this temperature range. Since the purge flow at the conditions used for purge-and-trap analysis results in only 300 mL of purge flow (30 mL/min for 10 min), no breakthrough problems are expected for the polar volatile compounds unless the sample contains high levels of purgeable materials in the same volatility range as acetone. Assuming a 50 percent purging efficiency for acetone, the 560 mL breakthrough volume for 1.0 µg of acetone translates to a possible upper limit of about 400 µg/L for 5.0 mL samples. The 400 mL

breakthrough volume for 10.0 µg of acetone (corresponding to 4000 ug/L) definitely does not provide a comfortable margin relative to the 300 mL purge volume used. Further work is necessary to accurately determine maximum acetone levels for this method with field samples.

Since the purging efficiency results for epichlorohydrin indicate that propylene oxide might require the 85°C purge temperature for effective recovery, the breakthrough experiments for propylene oxide were repeated using 85°C purge gas equilibration and the all-Tenax trap. With the trap at 21° to 25°C, the breakthrough volume for 1.0 mL injections of aqueous propylene oxide standards averaged 400 ± 30 mL for 1.0 µg samples (quadruplicate) and 320 ± 40 mL for 10 µg samples (triplicate). Since the adopted purge conditions are 30 mL/min for 10 min, trap breakthrough for propylene oxide at reasonable levels is not expected to present any analytical difficulty. However, this analyte might display significantly greater trap overload induced breakthrough than acetone due to its lower boiling point, and this result may indicate that propylene oxide is best analyzed with room temperature purging and the 3-component trap.

Purging and Desorption Efficiency

The results of the purging and desorption efficiency experiment for the nonpolar compounds are shown in Table 33 and those for the polar compounds are shown in Table 34. In the latter case, purging efficiency was checked at both room temperature and 85°C.

For the nonpolar analytes, all except propylene oxide and methyl mercaptan were recovered essentially quantitatively through the purge/trap/desorb cycle. Both propylene oxide and methyl mercaptan were poorly recovered from the trap with about 2/3 of the propylene oxide and 1/2 of the methyl mercaptan apparently lost to decomposition during the trap desorption step. Assuming that the trap desorption losses were the same for the purge/trap/desorb data as for the nonpurge/trap/desorb data, one can compute purging efficiencies of about 75 percent for methyl mercaptan and about 25 percent for propylene oxide.

TABLE 33. PURGING AND DESORPTION EFFICIENCY RESULTS FOR NONPOLAR VOLATILE COMPOUNDS

Compound	Spike Level, µg/L)	Average[a] Percent Recovery ± Standard Deviation (vs. Septum Injection	
		Room Temperature Purge/trap/desorb	Non-purge/ trap/desorb
Methyl mercaptan[c]	500	37 ± 7	49 ± 4
Propylene oxide	100	8.8 ± 0.7	37 ± 7 (33 ± 0.6)[b]
Allyl chloride	100	100.6 ± 0.8	100.6 ± 1.0
Ethyl ether	100	92.1 ± 1.6	102.2 ± 0.8
Isoprene	100	105 ± 2	102 ± 2
Cyclohexane	100	96 ± 3	82 ± 5
Xylene	100	96 ± 2	94 ± 3

(a) Average of three replicates.
(b) Average and deviation from the mean after rejection of one replicate that may be an outlier.
(c) Data obtained separately from the other compounds due to the necessity to avoid methanol which interferes chromatographically.

TABLE 34. PURGING AND DESORPTION EFFICIENCY RESULTS FOR POLAR VOLATILE COMPOUNDS

Compound[b]	Average[a] Percent Recovery ± Standard Deviation (vs. Septum Injection)		
	80°C Purge/trap/desorb	Room Temperature Purge/trap/desorb	Nonpurge/ trap/desorb
Acetone	87 ± 6	12 ± 3	107 ± 2
Allyl alcohol	12 ± 6	0.6 ± 0.1	87 ± 3
Methyl ethyl ketone	94 ± 4	15 ± 4	105 ± 2
Epichlorhydrin	23 ± 23	0.0	21 ± 8
Dioxane	15 ± 8	1.8 ± 0.2	87 ± 3
Vinyl acetate	46 ± 37	15 ± 18	48 ± 19
Methyl isobutyl ketone	100 ± 1	39 ± 8	105 ± 2
2-Hexanone	96 ± 3	23 ± 9	102 ± 2
Butyl acetate	70 ± 17	34 ± 21	81 ± 18
Amyl acetate	60 ± 32	20 ± 22	66 ± 19

(a) Each value represents the average of three replicates.
(b) All compounds spiked at 100 µg/L.

For the polar analytes (Table 34) a number of conclusions can be made:

- Of all the analytes only methyl isobutyl ketone could be considered for analysis using a room temperature purge. The others have purging efficiencies that are too low and, in some cases, have unacceptably poor precisions. It is noteworthy that dioxane, recovered at only 1.8 percent, nevertheless, had surprisingly good precision (10 percent RSD)

- The best performance both in method efficiency and precision is observed for the four ketones which are essentially recovered quantitatively with precisions ranging from 1 to 7 percent RSD using heated purge-and-trap

- The three acetate species all display mediocre recoveries (40 to 70 percent) and very poor precisions (25 to 70 percent RSD). It is clear from the nonpurge/trap/desorb results that the difficulty with these compounds is not associated with purging efficiency, and that, indeed, they are apparently purged with 100 percent efficiency. Probably, these compounds are being hydrolyzed during the desorption step since the analysis method used does not include a trap drying step. If a trap drying step were used and, indeed, would prevent this decomposition, both butyl and amyl acetate could probably be analyzed with room temperature purging

- The poor recoveries of dioxane and allyl alcohol are due almost exclusively to a low purging efficiency (10 to 15 percent) at 85°C

- Epichlorohydrin, like the acetates, is apparently purged quantitatively at 85°C since the 85°C purge recovery is the same as the nonpurge/trap/desorb result. However, the very low overall recovery (20 percent) clearly indicates loss of this compound during desorption, probably by hydrolysis.

Estimation of Detection Limit

Replicate analyses of 5-mL purged reagent water standards at levels near the detection limit were quantified against purge

calibration standards spanning an order of magnitude of concentration range and encompassing the detection limit spiking level used. The results of these experiments are shown in Table 35 (nonpolar compounds) and Table 36 (polar compounds). Propylene oxide is included in both sets of data, since the room temperature purging efficiency experiments indicated it might be better analyzed with 85°C purging.

Methyl mercaptan was not included in the analyses for Table 35 because the preceding work showed that it was not well suited to FID detection. A serious problem with methyl mercaptan is that it and methanol interfere under the chromatography conditions used. In addition, the early section of the FID chromatograms contain baseline disturbances ("humps") on which methyl mercaptan elutes and which are variable and substantially complicate the problem of methyl mercaptan quantification. These chromatographic difficulties together with the low and possibly variable methyl mercaptan FID response factor (for example, the FID is 28 times as responsive for directly injected isoprene than for methyl mercaptan) and the poor purge/trap/desorb recovery of methyl mercaptan (Table 33) indicate a rather high method detection limit (MDL) for this compound using FID. For that reason, a multiple replicate MDL was not assessed for methyl mercaptan, although some early experiments indicated the MDL would be in the range of 50 to 100 µg/L. Our conclusion, therefore, is that a Hall detection system in the sulfur specific mode offers far greater promise for acceptable analytical performance for methyl mercaptan. Results of the MDL determination for the remaining nonpolar analytes are shown in Table 35. Because of the desorption decomposition and low purging efficiency of propylene oxide, the MDL value for this compound (1.5 µg/L) is 15-fold higher than those for the other compounds (0.1 µg/L). Nevertheless, this propylene oxide MDL value compares well with that found for 85°C purging (Table 36). A chromatogram of one of the detection limit replicates of Table 33 is shown in Figure 16. As is clear from this chromatogram, spiking levels lower by a factor of 2 to 3 would have been more appropriate to assess the detection limit for these compounds, and

TABLE 35. RESULTS OF DETECTION LIMIT STUDY FOR NONPOLAR VOLATILE COMPOUNDS

Compound	P&T Calibration Standards(a)	Analysis Results for Detection Limit Sample, Five Replicates			
	Average Response Factor ± SD(%RSD)(b)	Spike Level, µg/L	Level Found ± SD(%RSD)(b)	Percent Recovery ± SD(b)	Estimated MDL,(c) µg/L
Propylene oxide	40 ± 4 (10)	4.0	4.3 ± 0.4 (9)	108 ± 10	1.5
Allyl chloride	8.1 ± 0.2 (2)	1.0	0.97 ± 0.02 (2)	97 ± 2	0.1
Ethyl ether	7.1 ± 0.2 (3)	1.0	0.99 ± 0.03 (3)	99 ± 3	0.1
Isoprene	3.9 ± 0.2 (5)	1.0	0.94 ± 0.03 (3)	94 ± 3	0.1
Cyclohexane	3.3 ± 0.6 (18)	1.0	0.995 ± 0.016 (2)	100 ± 2	0.1
o-Xylene	3.9 ± 0.4 (11)	1.0	0.91 ± 0.03 (3)	91 ± 3	0.1

(a) Calibration levels: 0.6 µg/L (duplicate) 2.0 µg/L (duplicate) and 6.0 µg/L (single); propylene oxide at 4-fold higher level in each case.
(b) SD = Standard Deviation; %RSD = percent relative standard deviation; five replicates.
(c) MDL = Method detection limit; calculated using Student's t-value of 3.75 for 99 percent confidence and five replicates (4 degrees of freedom): MDL = SD x 3.75.

Data from which the results in this table were computed were produced on the same instrument on successive days by the same analyst. Calibration standards and spiked samples were prepared fresh each day.

TABLE 36. RESULTS OF DETECTION LIMIT STUDY FOR POLAR VOLATILE COMPOUNDS

Compound	Purge-and-Trap Calibration Standards: Levels in Calibration Standards, µg/L Low	Medium	High	Average External Standard Response Factors mean[c] ± SD (% RSD)[b]	Analysis Results for Detection Limit Sample: Spike Level, µg/L	Level Found, µg/L Mean[c] ± SD (% RSD)[b]	Percent Recovery ± SD	Estimated[d] Method Detection Limit µg/L
Methyl ethyl ketone	0.6	2.0	6.0	5.6 ± 1.0 (16)	1.0	0.92 ± 0.06 (6)	92 ± 6	0.3
Methyl isobutyl ketone	0.6	2.0	6.0	5.1 ± 0.3 (6)	1.0	1.02 ± 0.04 (4)	102 ± 4	0.3
2-Hexanone	0.6	2.0	6.0	5.4 ± 0.3 (6)	1.0	0.96 ± 0.12 (12)	96 ± 12	0.6
Butyl acetate	0.6	2.0	6.0	6.9 ± 0.3 (4)	1.0	0.96 ± 0.18 (19)	96 ± 18	1
Amyl acetate	1.2	4.0	12	8.4 ± 1.2 (14)	2.0	2.2 ± 0.4 (18)	110 ± 20	2
Acetone	3.0	10	30	7.6 ± 1.2 (16)	5.0	6.3 ± 0.8 (13)	126 ± 16[e]	4
Propylene oxide	3.0	10	30	16 ± 4 (25)	5.0	5.9 ± 1.1 (19)	118 ± 22	5
Vinyl acetate	3.0	10	30	17 ± 3 (18)	5.0	5.3 ± 0.4 (9)	106 ± 10	2
Dioxane	6.0	20	60	98 ± 30 (31)	10	15 ± 2 (14)	150 ± 21[e]	10
Epichlorohydrin	6.0	20	60	82 ± 36 (44)	10	4 ± 2 (50)	40 ± 20	10
Allyl alcohol	30	100	300	112 ± 40 (36)	50	78 ± 14 (18)	156 ± 28	70

(a) Each standard was analyzed once
(b) SD = standard deviation; % RSD = percent relative standard deviation
(c) Average of triplicate analysis
(d) Estimated to be five times the standard deviation.
(e) Includes uncorrected area contributions from blank.

Data from which the results in this table were computed were produced on one instrument in a single day by one analyst. Calibration standards and spiked samples were prepared fresh on the day of analysis.

the estimated MDL of Table 35 should be interpreted with that fact in mind.

It is clear from the precison values shown for the polar compounds in Table 36 that the levels chosen for these analyses were indeed near the MDL levels. Not surprisingly, compounds for which poor purging efficiency or poor desorption recovery are demonstrated by Table 34 have relatively high estimated detection limits. The only unexpected result of Table 36 is the significantly worse performance of allyl alcohol compared to the other analytes for which the Table 34 results indicate possible hydrolysis. As is obvious from Figure 17, the very severe GC peak tailing observed for allyl alcohol is the reason for its significantly higher detection limit. Based on the appearance of the Figure 17 chromatogram, quantification of allyl alcohol by peak height rather than peak area might be expected to give a MDL in the range of 15 to 30 µg/L. Additionally, the somewhat variable background levels in the reagent water of species which coelute with acetone and dioxane had the effect of increasing the uncertainty levels of the response factors for these two species. Quantifying these background species in data obtained for reagent water blanks with the corresponding response factors for acetone and dioxane results in levels of about 1 and 6 µg/L, respectively. These background levels account for the greater than 100 percent recoveries in the detection limit replicates of these two analytes since correction for background levels was not performed on the results shown in Table 36.

CONCLUSIONS

Some analytical problems were encountered with all three of the high-interest analytes, propylene oxide, methyl mercaptan and allyl alcohol. Propylene oxide can be analyzed by either the room temperature or 85°C purge-and-trap approach. However, the propylene oxide data clearly indicate that this compound partially decomposes during trap desorption, and the result is that variable precision and accuracy might be expected without further method improvements. Indeed, most of the

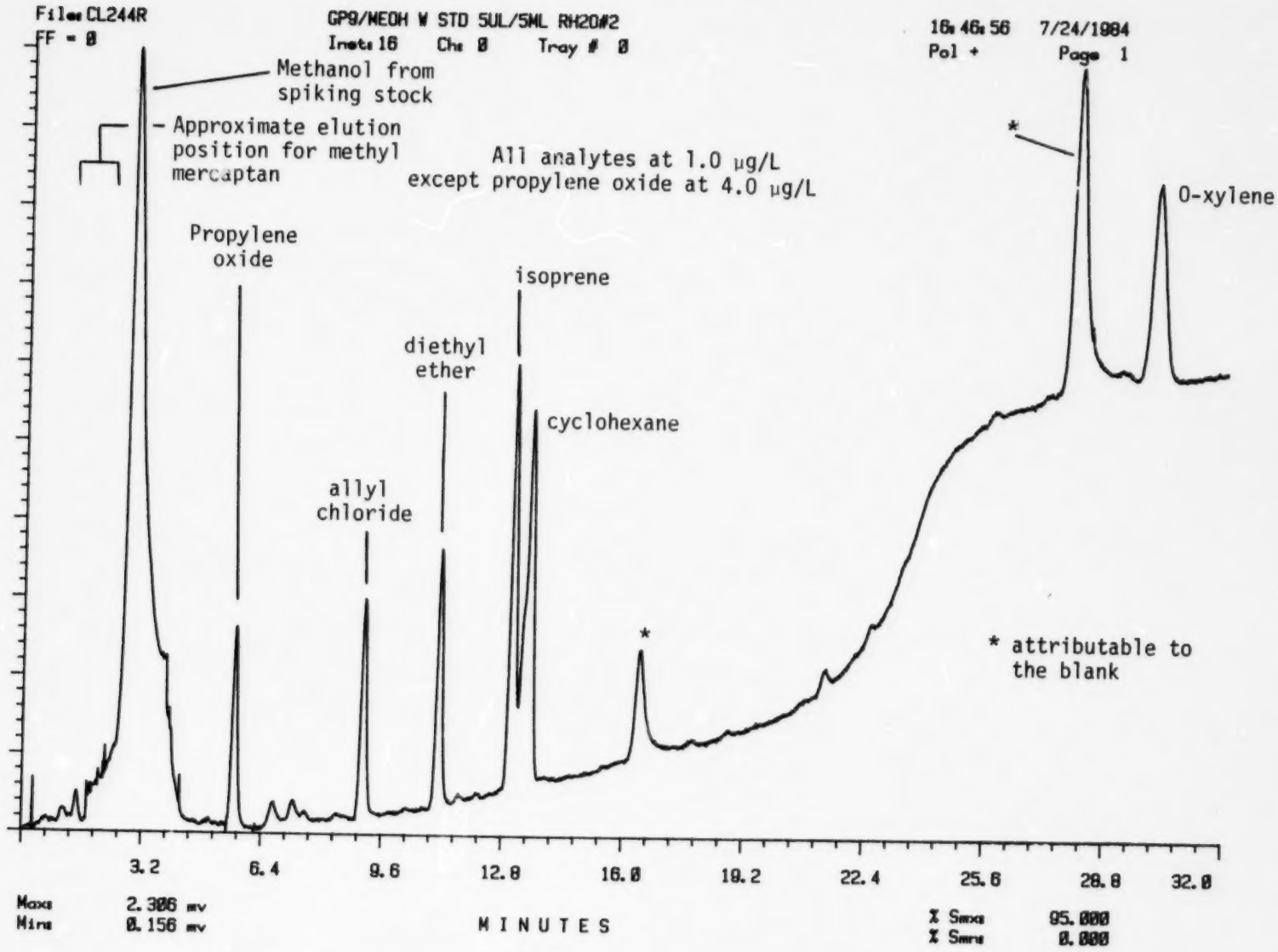

Figure 16. GC-FID chromatogram of a standard used for assessment of the method detection limit for nonpolar volatile compounds

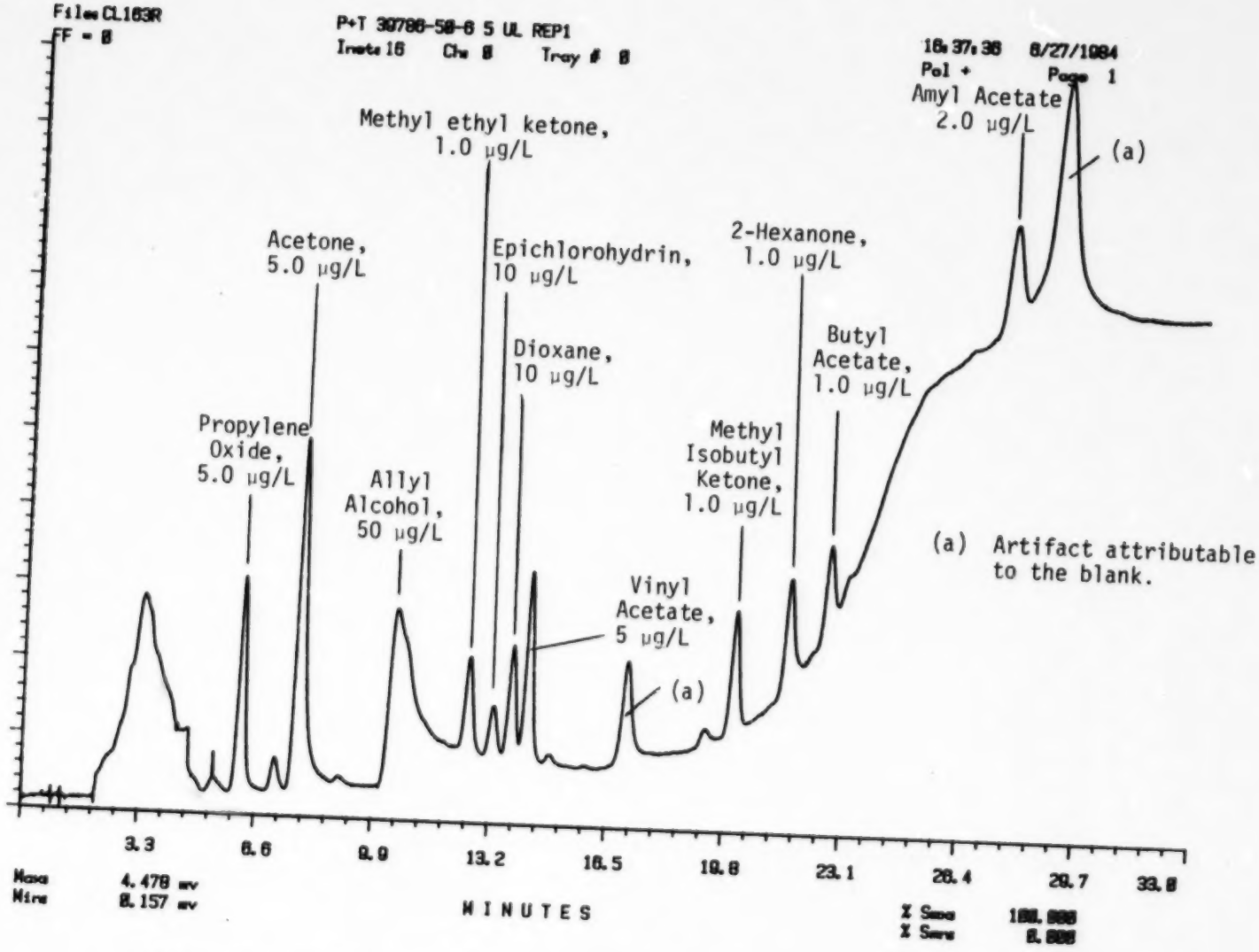

Figure 17. GC-FID chromatogram for polar volatile compounds of a standard used for assessment of the method detection limit.

problems associated with the purge-and-trap analyte sets were shown to be associated with decomposition, probably by hydrolysis, during trap desorption. Two additional problems were encountered with methyl mercaptan: (1) FID sensitivity was low, as expected, and (2) coelution with methanol, often present as a laboratory contaminant or spiking medium, significantly reduced its reproducibility. Both of these problems could be eliminated with a sulfur-specific detector. In the case of allyl alcohol, the modified Method 603 scheme suggested a detection limit on the order of 70 µg/L. This result was due to the very low purging efficiency (about 15 percent) at 85°C and the extreme GC peak tailing on the Method 601 column.

RECOMMENDATIONS

- Future method development effort for methyl mercaptan should involve a sulfur-specific detector such as the Hall electrolytic conductivity detector. A purge-and-trap approach will probably prove workable for methyl mercaptan

- Future method development for allyl alcohol should include a capillary or polar packed column determinative step to avoid GC peak tailing. A heated purge-and-trap approach is recommended, even though the purging efficiency is low

- Storage stability of hydrolyzable analytes such as esters and epoxides in field sample matrices must be investigated before a heated purge-and-trap approach for them can be finalized. The predominant factor controlling storage stability is expected to be pH

- The usefulness of a trap drying step, either preceding or during trap desorption, should be investigated to reduce variability caused by hydrolysis of esters and epoxides during trap desorption.

SECTION 9

VOLATILE AMINES AND ALCOHOL AMINES

The volatile amines evaluated in this work included the following:

Methylamine	Diethylamine
Trimethylamine	Triethylamine
Ethylamine	Butylamine

Methylamine is the only volatile amine tested which is not a high-interest compound. The alcohol amines tested included two high-interest compounds: ethanolamine and isopropanolanine.

EXPERIMENTAL

Chromatographic Separations

Chromatographic characteristics of the six volatile amines and the two alcohol amines were initially investigated on two fused silica capillary columns and two packed columns:

Quadrex, Carbowax 20M, 0.25 µm film, 25 m by 0.25 mm ID, fused silica

J&W, DB-5, 0.25 µm film, 30 m by 0.25mm ID, fused silica

Porapak QS, 80/100 mesh, 10 ft by 2mm ID, glass

1 percent SP1000/Carbopak B, 60/80 mesh, 6 ft by 2mm ID, glass

The instrument used for the capillary column work was a Hewlett-Packard 5890A operated with hydrogen carrier (50 cm/sec at 40°C) in the split injection mode with the standard injector liner for split mode (split ratio 20:1). For the packed column work, a Varian 1400 with helium carrier at 30 mL/min (flow controlled) was used. Both instruments were operated in the FID mode.

Stock solutions of the individual compounds were prepared in tetraglyme at 100 mg/mL. Working standards of the individual compounds were prepared at the 100 µg/mL level in pentane and carbon disulfide and at the 100 µg/mL level in decane for the capillary column work. Aqueous working standards of individual compounds were prepared at 100 µg/mL from the tetraglyme stocks, and these standards were used for the packed column work. Vapor samples were prepared by introducing an uncontrolled amount of the gaseous reagents (methylamine, ethylamine and trimethylamine) or 10 µL of the neat liquids (diethylamine, triethylamine and butylamine) through the septum of a 10-mL vial. Injection volumes of working standards in organic solution were 2.0 µL for both capillary and packed column systems. Gas injection volumes were 100 to 200 µL. In later work, the Hewlett-Packard 5890A GC was fitted with a Quadrex fused silica capillary column (50 m by 0.32mm ID, 5.0 µm OV-1) and the split injection port liner was modified by removing the GC packing material. The oven temperature was programmed from a room temperature injection at 6°C/min for capillary column analyses and at 8°C/min for packed column analyses.

A special column packing for volatile amine analysis was also investigated[5]. Carbopack B, 60/80 mesh was worked through a 100 mesh standard sieve using a soft brush. This material was pre-treated with KOH/methanol to provide a loading level of 0.3 percent KOH on the packing. The KOH/methanol (0.10 to 0.15 percent) just covered the packing material in a petri dish. The methanol was allowed to evaporate with gentle stirring in the draft of a fume hood and then finally dried at 100°C. The dried, KOH-treated packing was re-sieved at 100 mesh and then coated with Carbowax 20M in CH_2Cl_2 at a 4.8 percent loading level using the procedure above with final drying at 70°C for 1.5 hours. After final sieving to obtain a 100/120 mesh size, a 6 ft x 2mm glass column was packed and conditioned at 220°C. The column was further conditioned with 30 5-µL injections of water over 10 min at 220°C before injection of amine standards. Individual aqueous stock solutions of the amines at 1.0 percent (w/v) were used to prepare individual and mixed aqueous standards at the 100 µg/mL level. Standards were analyzed

using 2 µL injections and the packed column GC conditions given above except that initial GC oven temperatures ranging from 50°C to 80°C were tested.

Purge-and-Trap Feasibility Study

The Tekmar LSC-2 was connected directly to the FID detector in configurations which allowed checking the adsorption characteristics of the volatile amines in the transfer lines from the LSC-2 to the GC, the transfer lines from the purge vessel to the LSC-2, the LSC-2 6-port valve, and the adsorption/desorption trap. Aqueous standards of individual compounds at 1.0 mg/mL containing no ammonia, about 5:1 ammonia:analyte, and about 1:5 ammonia:analyte were used. Generally, 1.0 µL sample injections were made through a septum-equipped T-fitting into the flowing purge stream. In some cases, injections were made into a disassembled fitting in a stopped-flow mode. The traps tested were the 3-component and all-Tenax traps described for the volatile compounds, as well as a trap packed 2/3 with Tenax at the inlet and 1/3 with activated charcoal removed from an EPA VOST trap. Trap adsorption was always at room temperature and desorption was always at 180°C. The gas flow through the LSC-2 was helium at 30 mL/min. For adsorption/desorption checks, the adsorption time was always 10 min (300 mL volume), the desorption time 5 min, and the trap bake time, 5 min at 210°C.

Heated Headspace Sampling Feasibility Study

Amine analysis using automated heated headspace sampling (HHS) for the volatile amines was examined using a Perkin-Elmer Sigma 2000 GC (with FID detector) interfaced to a Perkin-Elmer HS-100 auto HHS unit. The same Quadrex fused silica capillary column (5.0 µm OV-1 film) described previously was used. The analysis conditions were:

- Helium carrier at 30 cm/sec (17 psi)
- GC program: 20°C for 3 min, programmed to 100°C at 6°/min

- o Sample equilibration, 15 min at 90°C
- o Injection time, 0.08 min
- o Split ratio, 4:1

Aqueous samples were prepared at the 1 mg/L level singly and as mixtures using 1 percent aqueous stocks and analyzed in triplicate. Typically, a 10-mL sample in the standard autosampler vial (22 mL) was acidified with 1 mL of 4M NH_4Cl, frozen in dry ice and then sealed immediately after the addition of 5.0 g anhydrous Na_2SO_4 and 0.2 to 0.3 gm reagent NaOH. After thawing, the sample was mixed thoroughly and analyzed using the conditions given above.

RESULTS AND DISCUSSION

Chromatographic Separations

No GC peaks were observed for any of the alcohol amines on any of the GC systems used except for the Carbowax 20M fused silica capillary column for which extremely wide, tailing peaks with widths at half heights of 90 to 120 sec were observed. The alcohol amines were not tested on the specially prepared packing (4.8 percent Carbowax 20M on 0.3 percent KOH-treated Carbopack B). However, it is doubtful that they could be eluted from that column. No GC peaks were observed for any of the amines on the Porapak QS column using either standards in pentane or gas sample injections (i.e., no solvent). GC peaks with reasonable retention values were obtained for all of the amines except butylamine using the 1 percent SP1000/Carbopack B column. However, all of the peaks were relatively broad and exhibited severe tailing even at the 200 ng injection level.

In testing the fused silica capillary columns, no GC peaks were obtained with the DB-5 column for any of the analytes for both decane solvent injection and 200 µL gas injections of the individual compounds. The results for the Carbowax 20M column were also not definitive for either gas or solvent standard injections, since some broad peaks were detected for two analytes (the tertiary amines) but none for any others.

It was discovered after these experiments were concluded that the split-mode injector liner supplied with the H-P 5890A GC contained 2 percent OV-101 on Chromosorb W-HP rather than the usual silanized glass wool. It is possible that severe adsorption in this injector liner may have caused the apparent surprising absence of chromatographic capability observed for the amine analytes with the fused silica columns. However, very high level "loading" injections seemed not to have any effect on improving analyte throughput. In later work using the very thick film OV-1 capillary used for the heated headspace sampling investigations, the split-mode injector liner was used without packing, and direct injection of the amine mix resulted in good separation of all six compounds with acceptable tailing of the highest polarity primary amines (asymmetry factor 1:4 at 10 percent peak height).

The separation obtained with the special column tested is shown in Figure 18. This column, which is 4.8 percent Carbowax 20M on 0.3 percent KOH-treated Carbopack B, 100/120 mesh, seemed to be very reliable and rugged for direct aqueous injection. Based on the Figure 18 chromatogram, a 5-µL direct aqueous injection analysis using a nitrogen specific detector would be expected to achieve a detection limit on the order of 200 to 800 µg/L. Due to the very high boiling points and polarities of the alcohol amines, these compounds could not be expected to elute from this column, and, therefore, they were not tested on it.

Purge-and-Trap Feasibility Study

The sample transfer lines and six-port valve of the Tekmar LSC-2 sample concentration device displayed a moderate capacity for adsorption of the analytes at the 0.2 and 2.0 µg levels when 2 µL aqueous samples were injected into the purge vessel exit line. Addition of NH_3 to the sample decreased the degree of adsorption for the lower level standards. It is doubtful that levels below 0.5 to 0.2 µg of the more polar primary amines can be recovered from the LSC-2 with its standard plumbing configurations. Use of standard adsorption traps showed, not surprisingly, that the amines could not be recovered from the three-

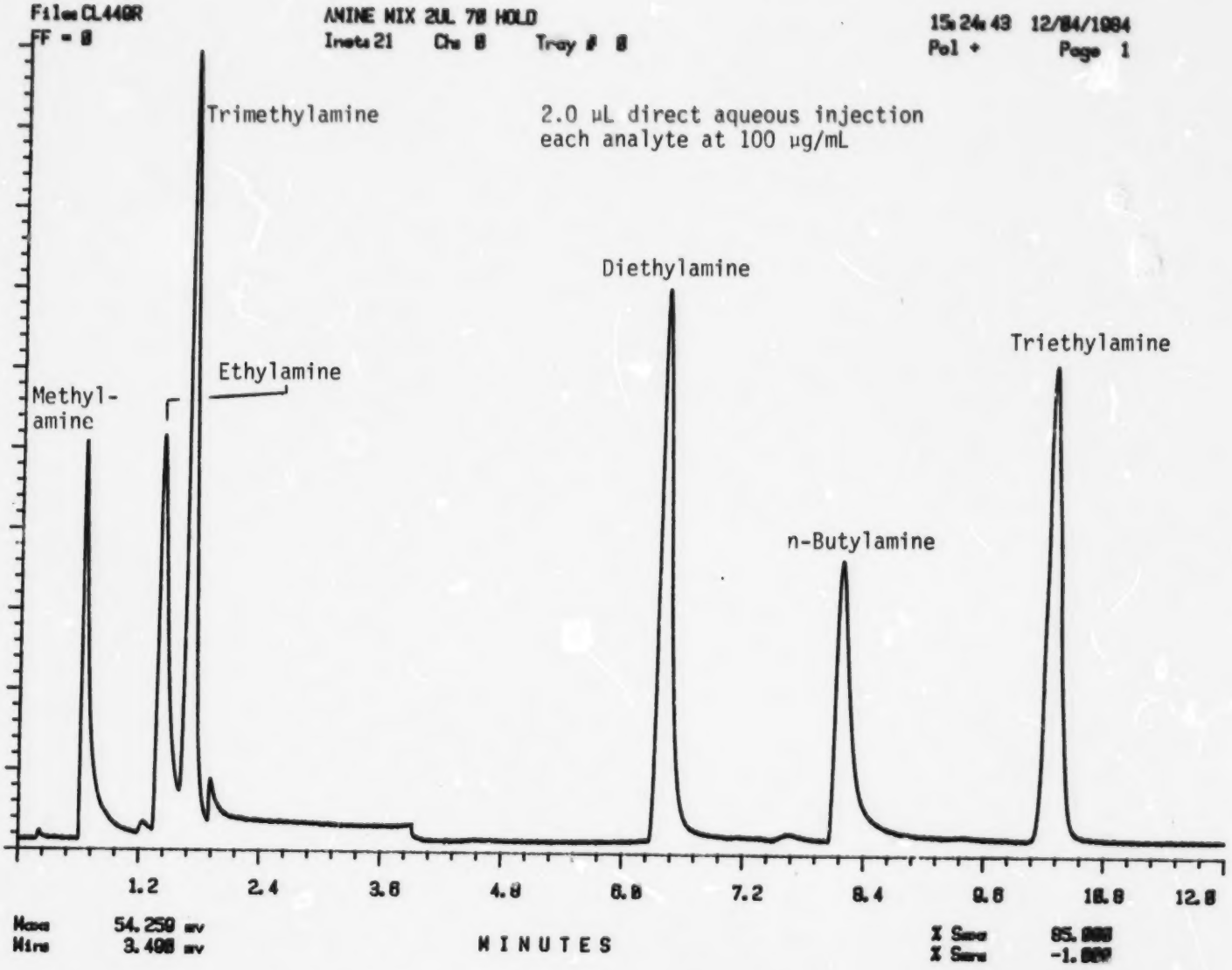

Figure 18. GC-FID chromatogram of volatile amines on 4.8 percent Carbowax 20M/0.3 percent KOH-Carbopack B.

component trap. The all-Tenax trap successfully trapped and desorbed all of the amines, but methylamine, trimethylamine, and ethylamine broke through this trap under the flow conditions used (30 mL/min for 10 min). The third trap tested was packed with a type of granular activated carbon used in the EPA VOST sampler. None of the amines broke through this trap, but they displayed very poor (less than 10 percent) desorption recoveries. Based on the trap/desorption results for the 2.0 µg samples, a purge-and-trap approach for the volatile amines would require some further development work to prevent adsorption of these compounds in the plumbing of the purge/trap/desorb device. Two possibilities include alkali treatment and substitution of Teflon or fused silica tubing for all of the stainless steel tubing. Substitution of an all-Teflon six-port valve for the standard stainless steel/vespel one might also be required. A trap from which the amines could be successfully desorbed possibly could be prepared using a Carbopack support and a strongly basic modifier such as polyethylenimine. A KOH-treated trap might not work well with a heated purge-and-trap approach due to the relatively large amount of water transferred to the trap during purging.

Heated Headspace Sampling Feasibility Study

Poor results obtained for all but the tertiary amines with HHS and thick-film (OV-1) capillary chromatography are probably due to adsorptive activity of the metal sampling device and transfer lines. GC peak shape and throughput improved dramatically after repeated sampling of a sample vial containing only neat silanizing reagent (hexamethyldisilazane). Since GC analysis of the amines by direct injection on a second, identical column produced good peak shapes, it is inferred that the improvement in the HHS system was due more to deactivation of the sampling device than to deactivation of the GC column. An example chromatogram obtained from analysis by HHS of a 10-mL sample containing all six amines at the 100 µg/L level is shown in Figure 19. Excellent response for the two tertiary amines but extremely poor response for diethylamine and no response for the three primary

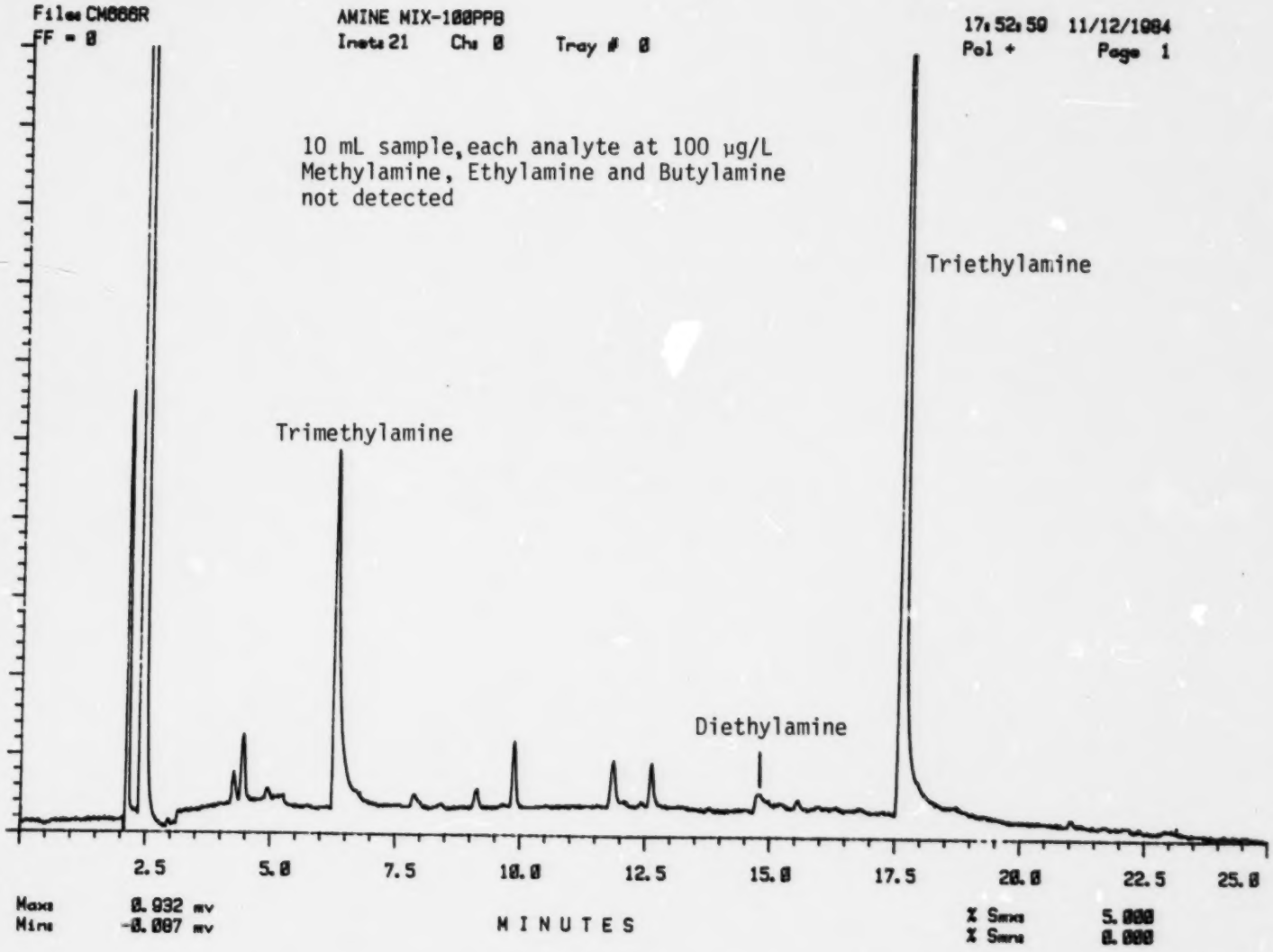

Figure 19. GC-FID chromatogram from heated headspace sampling of volatile amines

amines is probably due more to the transfer line adsorption activity than to a poor liquid/gas phase partition ratio even though the primary amines are expected to display a significantly lower portion ratio than tertiary amines of about the same volatility. This explanation is supported by the severe tailing of the diethylamine peak. Since a direct septum injection on the column that provided the Figure 19 chromatogram was not performed, a chromatographic cause for the peak tailing and non-response to the primary amines cannot be ruled out. With improvements in deactivation of the HHS sampler and transfer lines and the use of a nitrogen-selective detector, tertiary amine detection limits below 10 µg/L for 10-mL samples ought to be achievable. Performance characteristics for primary and secondary amines cannot be predicted at the present time due to the preliminary nature of these results. The attempt to drive the aqueous/headspace equilibrium toward the gas phase through the use of near-saturation Na_2SO_4 for salting out and the high (90°C) pre-sampling equilibrium temperature, together with the use of high levels of NH_3 to act as a carrier (to minimize sampling device and chromatography adsorption) are thought to be the only sample treatment options available for detection limit enhancement. No response factors or calibration curves were generated in these range-finding experiments. However, analysis of triplicate samples at 10-fold lower levels than those for Figure 19 show the two trialkyl amines to be near their detection limits.

CONCLUSIONS

Based on extensive work, an 85°C purge/trap/desorb approach to volatile amine analysis has no merit and should not be pursued further. The HHS approach that was studied seems to have some merit, especially with a nitrogen selective detector, but extensive modification of the sampler device on the Perkin-Elmer HS-100 would be required to eliminate all contact of the vapor sample with metal surfaces. The GC peak tailing observed for these very polar, basic species is acceptable using specially prepared packings or thick film capillary columns (for example, Figure 19).

No progress was made on GC analysis of the extremely polar alcohol amines, and without a chromatographic determinative technique, no experiments on extraction/sample workup were possible.

RECOMMENDATIONS

Future method development work for amines and alcohol amines should include ion chromatography with and without an ion exchange, distillation or evaporative pre-concentration step. For example, Sevenich and Fritz (6) have demonstrated ion chromatography separation of methylamine, dimethylamine, diethylamine, triethylamine, ethanolamine, hydrazine, hydroxylamine and others on Benson A104 using conductivity detection with an acidified mobil phase. Future work on purge-and-trap based methods for amines must address the fairly difficult problems of analyte adsorption in the transfer lines and the identification of an appropriate trapping medium from which nanogram levels can be reliably desorbed. For GC-based methodology, future work on a HHS approach has some merit, but it also must address the problem of adsorption on metalic parts of the sampling system and transfer line. Polar thick film fused silica capillary columns may perform better than the nonpolar column used in this work, and they are recommended for future GC based methods for these compounds. All GC based method development should be designed to use nitrogen-specific detection.

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APPENDIX A

TABLE V OF APPENDIX D TO 40 CFR 122

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TABLE V—*Toxic Pollutants and Hazardous Substances Required to be Identified by Existing Dischargers if Expected to be Present.*

Toxic Pollutants

Asbestos

Hazardous Substances

Acetaldehyde
Allyl alcohol
Allyl chloride
Amyl acetate
Aniline
Benzonitrile
Benzyl chloride
Butyl acetate
Butylamine
Captan
Carbaryl
Carbofuran
Carbon disulfide
Chlorpyrifos

Coumaphos
Cresol
Crotonaldehyde
Cyclohexane
2,4-D (2,4-Dichlorophenoxy acetic acid)
Diazinon
Dicamba
Dichlobenil
Dichlone
2,2-Dichloropropionic acid
Dichlorvos
Diethyl amine
Dimethyl amine
Dintrobenzene
Diquat
Disulfoton
Diuron
Epichlorohydrin
Ethanolamine
Ethion
Ethylene diamine
Ethylene dibromide
Formaldehyde
Furfural
Guthion
Isoprene
Isopropanolamine
Kelthane
Kepone
Malathion
Mercaptodimethur
Methoxychlor
Methyl mercaptan
Methyl methacrylate
Methyl parathion
Mevinphos
Mexacarbate
Monoethyl amine
Monomethyl amine
Naled
Napthenic acid
Nitrotoluene
Parathion
Phenolsulfanate
Phosgene
Propargite
Propylene oxide
Pyrethrins
Quinoline
Resorcinol
Strontium
Strychnine
Styrene
2,4,5-T (2,4,5-Trichlorophenoxy acetic acid)
TDE (Tetrachlorodiphenylethane)
2,4,5-TP [2-(2,4,5-Trichlorophenoxy) propanoic acid]
Trichlorofon
Triethylamine
Trimethylamine
Uranium
Vanadium
Vinyl Acetate
Xylene
Xylenol
Zirconium

APPENDIX B

COMMERCIAL SOURCES OF ANALYTES AND REAGENTS

The sources and purities of the reference compounds used are listed in Table B-1. The following reagents and chemical supplies were also used:

Methylene Chloride, Hexane, Methyl-t-butyl Ether, Methanol, Toluene, Diethyl Ether, and Acetone	Burdick and Jackson Laboratories
Sodium Sulfate:	J. T. Baker "AR"
Sulfuric Acid:	Mallinkrodt
Sodium Hydroxide:	J. T. Baker "AR"
Reagent Water:	Reagent water was prepared by passing boiled water from a Milli-RO/Milli-Q system through a column (40 cm x 2.8 cm ID) containing granular activated carbon with integral 300 mL reservoir. The column reservoir was protected from laboratory air with a drying tube filled with the same activated carbon
Granular Activated Carbon:	Barneby and Cheney Type PC, Lot 2547

TABLE B-1. SOURCES AND PURITIES OF ANALYTES AND REAGENTS

Compound	Supplier	Purity Percent[a]
Organophosphorous Compounds		
Chlorpyriphos	Chem Service	99
Coumaphos	Chem Service	98
Diazinon	Ciba Geigy	NS
Disulfoton	Chemagro	NS
Ethion	Chem Service	NS
Guthion	EPA	98.7
Malathion	American Cyanamid	Technical
Methyl parathion	Chem Service	98
Mevinphos	Chem Service	NS
Naled	Chem Service	92
Parathion	Monsanto	98.5
Trichlorfon	Chem Service	98
Neutral Nitrogen Compounds		
Benzonitrile	Chem Service	NS
Carbaryl	EPA	99.9
Carbofuran	FMC	NS
Dichlobenil	Chem Service	97
1,2-Dinitrobenzene	Aldrich	NS
1,3-Dinitrobenzene	Aldrich	NS
1,4-Dinitrobenzene	Aldrich	98
Diuron	Chem Service	NS
Methiocarb	Chem Service	99
Mexacarbate	Chem Service	95
2-Nitrotoluene	Chem Service	NS
3-Nitrotoluene	Chem Service	NS
4-Nitrotoluene	Eastman Kodak	NS
Chlorinated Pesticides		
Captan	Chevron	NS
Dichlone	Chem Service	98
Kepone	Chem Service	98
Methoxychlor	Sigma	98
Extractable Semivolatile Bases		
Aniline	Aldrich	99.5
Quinoline	Aldrich	96
Strychnine	Pierce	NS[b]

TABLE B-1. (Continued)

Compound	Supplier	Purity Percent[a]
Volatile Polar Compounds		
Acetone	Burdick & Jackson	NS[b]
Allyl alcohol	Aldrich	99
Methyl ethyl ketone	Burdick & Jackson	NS
Epichlorohydrin	Aldrich	99+
Dioxane	Burdick & Jackson	NS
Vinyl acetate	Aldrich	99+
Methyl isobutyl ketone	Aldrich	99.5
Methyl butyl ketone	Aldrich	99+
Butyl acetate	Aldrich	99+
Amyl acetate	Aldrich	99+
Purgeable Compounds		
Methyl mercaptan	Matheson	NS
Propylene oxide	Aldrich	99+
Allyl chloride	Aldrich	99
Ethyl ether[c]	Burdick & Jackson	NS
Isoprene	Aldrich	99+
Cyclohexane	Burdick & Jackson	NS
o-Xylene	Aldrich	97
Volatile Amines		
Methylamine	Matheson	NS
Trimethylamine	Matheson	NS
Ethylamine	Matheson	NS
Diethylamine	Chem Service	NS
Triethylamine	Chem Service	99+
Butylamine	Chem Service	99+
Alcohol Amines		
Ethanolamine	Chem Service	95
Isopropylamine	Chem Service	NS

(a) As given by supplier.
(b) NS = not specified by supplier
(c) Without preservative.